PATENT

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APPLICATION FOR UNITED STATES LETTERS PATENT

for

DYEING COMPOSITION COMPRISING A CATIONIC TERTIARY PARA-PHENYLENEDIAMINE AND A POLYMER CONTAINING A FATTY CHAIN, METHODS AND USES

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EXPRESS MAIL MAILING LABEL

NUMBER EV 323285803 US

DATE OF DEPOSIT December 12, 2003

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to French Application No. 02/15766 filed 13 December 2003, and further claims the benefit of U.S. Provisional Application No. 60/450,338 filed 28 February 2003, the entire disclosures of which are incorporated herein by reference in their entirety.

BACKGROUND OF THE INVENTION

The subject of the present application is a dyeing composition for dyeing keratinous fibres, in particular human keratinous fibres such as hair, comprising, in an appropriate dyeing medium, at least one cationic tertiary para-phenylenediamine containing a pyrrolidine ring, and at least one particular polymer containing a fatty chain.

The subject of the invention is also the use of this composition for dyeing keratinous fibres and the dyeing method using this composition.

It is known to dye keratinous fibres, and in particular human hair, with dyeing compositions containing oxidation dye precursors, generally called oxidation bases, such as ortho- or para-phenylenediamines, or ortho- or para-aminophenols and heterocyclic compounds. These oxidation bases are colourless or weakly coloured compounds which, when combined with oxidizing products, can give rise, through a process of oxidative condensation, to coloured compounds.

It is also known that it is possible to vary the shades obtained with these oxidation bases by combining them with couplers or colour modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds such as indole compounds.

The variety of molecules used in the oxidation bases and couplers allows a rich palette of colours to be obtained.

The so-called "permanent" coloration obtained using these oxidation dyes should moreover satisfy a number of requirements. Thus, it should be without disadvantage from the toxicological point of view, it should make it possible to obtain shades in the desired intensity and should exhibit good fastness to external agents such as

light, adverse weather conditions, washing, permanent waving, perspiration and rubbing.

The dyes should also make it possible to cover grey hair, and should finally be as less selective as possible, that is to say it is possible to obtain the least possible colour variations along the length of the same keratinous fibre, which is in general differentially sensitized (that is to say damaged) between its tip and its root.

It has already been proposed, in patent application WO 02/45675, to use compositions for the oxidation dyeing of keratinous fibres comprising a cationic tertiary para-phenylenediamine containing a pyrrolidine ring.

These cationic tertiary para-phenylenediamines containing a pyrrolidine ring lead to compositions which exhibit a harmlessness which is generally considered better than the compositions containing conventional para-phenylenediamines. However, the shades obtained when these compositions are used are markedly less intense and markedly more selective, that is to say that the dyes obtained exhibit substantial variations in colorations as a function of the degree of sensitization of the various types of hair or of the various areas of the same hair. The fastness of these shades can also vary greatly according to the degree of sensitization. In addition, the colorations obtained are also often more grey, that is to say less chromatic.

SUMMARY OF THE INVENTION

Surprisingly and advantageously, the applicant has just discovered that it is possible to obtain novel compositions for dyeing keratinous fibres, in particular human keratinous fibres such as hair, capable of overcoming the disadvantages cited above and in particular of leading to colorations with shades which are varied, chromatic, intense, aesthetic, not very selective and which withstand well the various attacks to which the fibres may be subjected, by combining, in the same composition, at least one cationic tertiary para-phenylenediamine containing a pyrrolidine ring and at least one particular polymer containing a fatty chain. In addition, these compositions exhibit a good toxicological profile.

The subject of the invention is therefore a dyeing composition for dyeing keratinous fibres comprising, in an appropriate dyeing medium, at least one cationic tertiary para-phenylenediamine

containing a pyrrolidine ring, and at least one polymer containing a fatty chain, as defined below.

The subject of the invention is also a dyeing method using this composition, and a multicompartment dyeing device or dyeing kit.

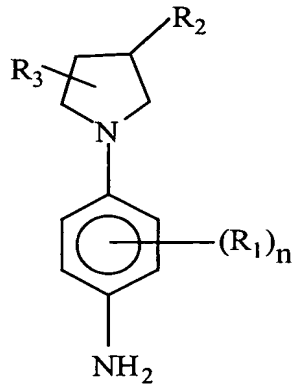
Another subject of the invention is the use of the composition of the present invention for dyeing keratinous fibres, in particular human keratinous fibres such as hair.

The composition of the present invention makes it possible in particular to obtain a chromatic coloration of keratinous fibres which is very intense, little selective and fast while avoiding degradation of these fibres.

Further purposes of the present invention, cationic tertiary para-phenylenediamine containing a pyrrolidine ring is understood to mean a para-phenylenediamine possessing an NH_2 group and in the para position thereof a di-substituted amine functional group whose substitutions form with the nitrogen a pyrrolidine ring, the molecule possessing at least one quaternarized nitrogen atom.

In the context of the present invention, the expression alkyl is understood to mean linear or branched radicals, for example methyl, ethyl, n-propyl, isopropyl, butyl and the like. An alkoxy radical is an alk-O radical, the alkyl radical having the definition above. Halogen preferably denotes Cl, Br, I, F.

Among the cationic tertiary para-phenylenediamines containing a pyrrolidine ring which can be used in the composition according to the present invention, there may be mentioned in particular the compounds of the following formula (I) and their addition salts.



(I)

in which

- n varies from 0 to 4, it being understood that when n is greater than or equal to 2, then the radicals R_1 may be identical or different,
- R_1 represents a halogen atom; a saturated or unsaturated, aliphatic or alicylic, C_1-C_6 hydrocarbon chain, it being possible for the chain to contain one or more oxygen, nitrogen, silicon or sulphur atoms or an SO_2 group, and it being possible for the chain to be substituted with one or more hydroxyl or amino radicals; an onium radical Z, the radical R_1 not containing a peroxide bond, or diazo, nitro or nitroso radicals,

R_2 represents an onium radical Z or a radical $-X-C=NR_8-NR_9R_{10}$ in which X represents an oxygen atom or a radical $-NR_{11}$ and R_8, R_9, R_{10} and R_{11} represent a hydrogen atom, a C_1-C_4 alkyl radical or a C_1-C_4 hydroxyalkyl radical,

R_3 represents a hydrogen atom or a hydroxyl radical.

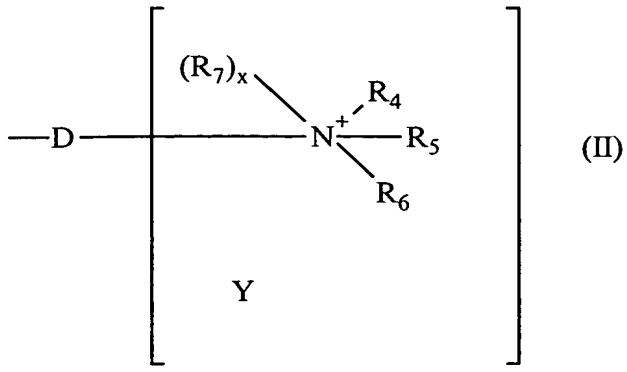
Onium denotes the quaternary radical of a nitrogenous base.

By way of example, R_1 may be a chlorine atom, a methyl, ethyl, isopropyl, vinyl, allyl, methoxymethyl, hydroxyethyl, 1-carboxymethyl, 1-aminomethyl, 2-carboxyethyl, 2-hydroxyethyl, 3-hydroxypropyl, 1,2-dihydroxyethyl, 1-hydroxy-2-aminoethyl, 1-amino-2-hydroxyethyl, 1,2-diaminoethyl, methoxy, ethoxy, allyloxy, or 2-hydroxyethyloxy radical.

In particular, n is equal to 0.

In formula (I), when n is equal to 1, R_1 is preferably a halogen atom; a saturated or unsaturated, aliphatic or alicylic, C_1-C_6 hydrocarbon chain, it being possible for one or more carbon atoms to be replaced with an oxygen, nitrogen, silicon or sulphur atom, or with an SO_2 group, the radical R_1 not containing a peroxide bond, or diazo, nitro or nitroso radicals. Preferably, R_1 is chosen from chlorine, bromine, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, C_1-C_4 aminoalkyl, C_1-C_4 alkoxy or C_1-C_4 hydroxyalkoxy radicals. By way of example, R_1 is chosen from a methyl, hydroxymethyl, 2-hydroxyethyl, 1,2-dihydroxyethyl, methoxy, isopropyloxy or 2-hydroxyethoxy radical.

The radical R_2 of formula (I) is, according to a particular embodiment, the onium radical Z corresponding to formula (II)



(II)

in which

- D is a single bond of a linear or branched C_1-C_{14} alkylene chain which may contain one or more heteroatoms chosen from oxygen, sulphur or nitrogen, and which may be substituted with one or more hydroxyl, C_1-C_6 alkoxy or amino radicals and which may carry one or more ketone functional groups;
- R_4, R_5 and R_6, taken separately, represent a C_1-C_{15} alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical; an aryl radical; a benzyl radical; a C_1-C_6 amidoalkyl radical; a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a C_1-C_6 aminoalkyl radical; a C_1-C_6 aminoalkyl radical in which the amine is mono- or di-substituted with a C_1-C_4 alkyl, (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; or
- R_4, R_5 and R_6 together, in pairs, form, with the nitrogen atom to which they are attached, a 4-, 5-, 6- or 7-membered saturated carbon ring which may contain one or more heteroatoms such as, for example, azetidine ring, a pyrrolidine ring, a piperidine ring, a piperazine ring, or a morpholine ring, it being possible for the cationic ring to be substituted with a halogen atom, a hydroxyl radical, a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a C_1-C_6 alkoxy radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, an amido radical, a carboxyl radical, a (C_1-C_6)alkylcarbonyl radical, a thio (-SH) radical, a C_1-C_6 thioalkyl (-R-SH) radical, a (C_1-C_6)alkylthio radical, an amino radical, an amino radical which is mono- or di-substituted with a (C_1-C_6)alkyl, (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical;
- R_7 represents a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; an aryl radical; a benzyl radical; a C_1-C_6 aminoalkyl radical; a C_1-C_6 aminoalkyl radical whose

amine is mono- or di-substituted with a (C_1-C_6)alkyl, (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; a C_1-C_6 carboxyalkyl radical; a C_1-C_6 carbamylalkyl radical; a C_1-C_6 trifluoroalkyl radical; a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a C_1-C_6 sulphonamidoalkyl radical; a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphinyl(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphonyl(C_1-C_6)alkyl radical; a (C_1-C_6)alkylcarbonyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylsulphonamido(C_1.C_6)alkyl radical;

- x is 0 or 1,

- when x = 0, then the linking arm is attached to the nitrogen atom carrying the radicals R_4 to R_6;

- when x = 1, then two of the radicals R_4 to R_6 form, together with the nitrogen atom to which they are attached, a 4-, 5-, 6- or 7-membered saturated ring and D is linked to the carbon atom of the saturated ring;

- Y is a counter-ion.

In formula (II), when x is equal to 0, then R_4, R_5 and R_6 separately are preferably chosen from a C_1-C_6 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a (C_1-C_6)alkoxy(C_1-C_4)alkyl radical, a C_1-C_6 amidoalkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, or R_4 with R_5 form together an azetidine ring, a pyrrolidine, piperidine, piperazine or morpholine ring, R_6 being chosen in this case from a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical; a C_1-C_6 aminoalkyl radical, an aminoalkyl radical which is mono- or di-substituted with a (C_1-C_6)alkyl radical, a (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; a C_1-C_6 carbamylalkyl radical; a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a (C_1-C_6)alkyl carboxy(C_1-C_6)alkyl radical; a (C_1-C_6)alkylcarbonyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)alkyl radical.

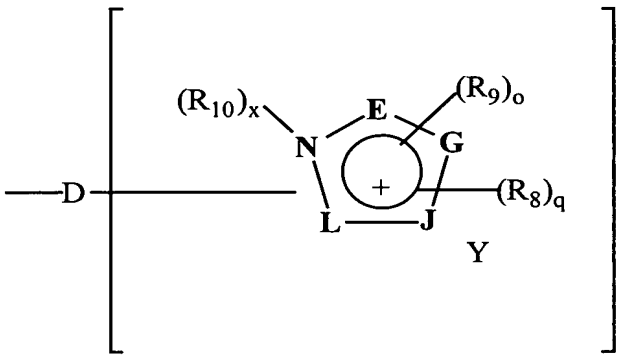
When x is equal to 1, then R_7 is preferably chosen from a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical, a C_1-C_6 aminoalkyl radical, a C_1-C_6 aminoalkyl radical whose amine is mono- or di-substituted with a (C_1-C_6)alkyl, (C_1-C_6)alkylcarbonyl, amido or a(C_1-C_6)alkylsulphonyl radical; a C_1-C_6 carbamylalkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical; a (C_1-

C_6)alkylcarbonyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)alkyl radical; R_4 with R_5 together form an azetidine, pyrrolidine, piperidine, piperazine or morpholine ring, R_6 being chosen in this case from a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; a C_1-C_6 aminoalkyl radical, a C_1-C_6 aminoalkyl radical whose amine is mono- or di-substituted with a (C_1-C_6)alkyl, (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; a C_1-C_6 carbamylalkyl radical; a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical; a (C_1-C_6)alkylcarbonyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)alkyl radical.

In the formula (II), D is preferably a single bond or an alkylene chain which may be substituted.

When the radical R_2 corresponds to formula (II), it is preferably a trialkylammonium radical whose alkyl radicals may be substituted.

According to a second embodiment, the radical R_2 represents the onium radical Z corresponding to formula (III)



(III)

in which

- D is a single bond or a linear or branched C_1-C_{14} alkylene chain which may contain one or more heteroatoms chosen from oxygen, sulphur or nitrogen, and which may be substituted with one or more hydroxyl, C_1-C_6 alkoxy or amino radicals, and which may carry one or more ketone functional groups;
- the vertices E, G, J, L, which are identical or different, represent a carbon, oxygen, sulphur or nitrogen atom to form a

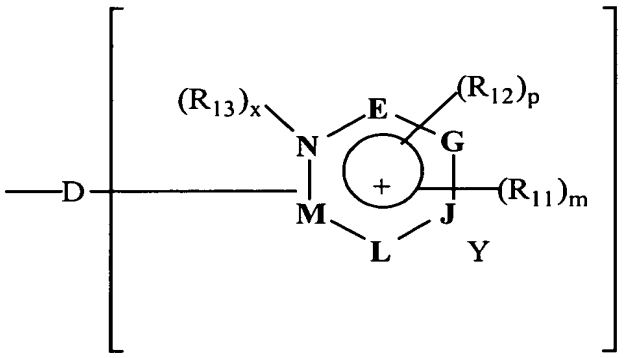
pyrrole, pyrazole, imidazole, triazole, oxazole, isooxazole, thiazole, isothiazole ring,

- q is an integer between 0 and 4 inclusive;
- o is an integer between 0 and 3 inclusive;
- q+o is an integer between 0 and 4;
- the radicals R_8, which are identical or different, represent a halogen atom, a hydroxyl radical, a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a C_1-C_6 alkoxy radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, an amido radical, a carboxyl radical, a C_1-C_6 alkylcarbonyl radical, a thio radical, a C_1-C_6 thioalkyl radical, a (C_1-C_6)alkylthio radical, an amino radical, an amino radical which is mono- or di-substituted with a (C_1-C_6)alkyl, (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; a C_1-C_6 monohydroxyalkyl radical or a C_2-C_6 polyhydroxyalkyl radical; it being understood that the radicals R_8 are carried by a carbon atom,
- the radicals R_9, which are identical or different, represent a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical, a C_1-C_6 carbamylalkyl radical, a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical, a benzyl radical; it being understood that the radicals R_9 are carried by a nitrogen,
- R_{10} represents a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; an aryl radical; a benzyl radical; a C_1-C_6 aminoalkyl radical, a C_1-C_6 aminoalkyl radical whose amine is substituted with a (C_1-C_6)alkyl, (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; a C_1-C_6 carboxyalkyl radical; a C_1-C_6 carbamylalkyl radical; a C_1-C_6 trifluoroalkyl radical; a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a C_1-C_6 sulphonamidoalkyl radical; a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphinyl(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphonyl(C_1-C_6)alkyl radical; a (C_1-C_6)alkylcarbonyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylsulphonamido(C_1-C_6)alkyl radical;
- x is 0 or 1
  - when x = 0, the linking arm D is attached to the nitrogen atom,
  - when x = 1, the linking arm D is attached to one of the vertices E, G, J or L,
- Y is a counter-ion.

The vertices E, G, J and L preferably form an imidazole ring.

Among the radicals R_2 of formulae (III), the preferred radicals are those in which x is equal to 0, D is a single bond or an alkylene chain which may be substituted.

According to a third embodiment, R_2 represents the onium radical Z corresponding to formula (IV)



(IV)

in which:

- D is a single bond or a linear or branched C_1-C_{14} alkylene chain which may contain one or more heteroatoms chosen from an oxygen, sulphur or nitrogen atom, and which may be substituted with one or more hydroxyl, C_1-C_6 alkoxy or amino radicals, and which may carry one or more ketone functional groups;
- the vertices E, G, J, L and M, which are identical or different, represent a carbon, oxygen, sulphur or nitrogen atom to form a ring chosen from the pyridine, pyrimidine, pyrazine, triazine and pyridazine rings;
- p is an integer between 0 and 3 inclusive;
- m is an integer between 0 and 5 inclusive;
- p+m is an integer between 0 and 5;
- the radicals R_{11}, which are identical or different, represent a halogen atom, a hydroxyl radical, a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a C_1-C_6 alkoxy radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, an amido radical, a carboxyl radical, a C_1-C_6 alkylcarbonyl radical, a thio radical, a C_1-C_6 thioalkyl radical, a (C_1-C_6)alkylthio radical, an amino radical, an amino radical which is substituted with a (C_1-C_6)alkyl, (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; a C_1-C_6

monohydroxyalkyl radical or a C_2-C_6 polyhydroxyalkyl radical; it being understood that the radicals R_{11} are carried by a carbon atom,

- the radicals R_{12}, which are identical or different, represent a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical, a C_1-C_6 carbamylalkyl radical, a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical, a benzyl radical; it being understood that the radicals R_{12} are carried by a nitrogen,
- R_{13} represents a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; an aryl radical; a benzyl radical; a C_1-C_6 aminoalkyl radical, a C_1-C_6 aminoalkyl radical whose amine is mono- or di-substituted with a (C_1-C_6)alkyl, (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; a C_1-C_6 carboxyalkyl radical; a C_1-C_6 carbamylalkyl radical; a C_1-C_6 trifluoroalkyl radical; a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a C_1-C_6 sulphonamidoalkyl radical; a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphinyl(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphonyl(C_1-C_6)alkyl radical; a (C_1-C_6)alkylcarbonyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylsulphonamido(C_1-C_6)alkyl radical;
- x is 0 or 1
  - when x = 0, the linking arm D is attached to the nitrogen atom,
  - when x = 1, the linking arm D is attached to one of the vertices E, G, J, L or M,
- Y is a counter-ion.

Preferably, the vertices E, G, J, L and M form, with the nitrogen of the ring, a pyridine and pyrimidine ring

When x is equal to 0, then R_{11} is preferably chosen from a hydroxyl radical, a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a C_1-C_6 alkoxy radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, an amido radical, a C_1-C_6 alkylcarbonyl radical, an amino radical, an amino radical which is mono- or di-substituted with a (C_1-C_6)alkyl, a (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; a C_1-C_6 monohydroxyalkyl radical or a C_2-C_6 polyhydroxyalkyl radical and R_{12} is chosen from a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical, a C_1-C_6 carbamylalkyl radical.

When x is equal to 1, R_{13} is preferably chosen from a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; a C_1-C_6 aminoalkyl radical, a C_1-C_6 aminoalkyl radical whose amine is mono- or di-substituted with a (C_1-C_6)alkyl radical, a (C_1-C_6)alkylcarbonyl radical, an amido radical, a (C_1-C_6)alkylsulphonyl radical; a C_1-C_6 carbamylalkyl radical; a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a (C_1-C_6)alkylcarbonyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)alkyl radical; R_{11} is chosen from a hydroxyl radical, a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a C_1-C_6 alkoxy radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, an amido radical, a C_1-C_6 alkylcarbonyl radical, an amino radical, an amino radical which is mono- or di- substituted with a (C_1-C_6)alkyl, (C_1-C_6)alkylcarbonyl, amido or (C_1-C_6)alkylsulphonyl radical; and R_{12} is chosen from a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical, a C_1-C_6 carbamylalkyl radical.

Preferably, R_{11}, R_{12} and R_{13} are alkyl radicals which may be substituted.

The radical R_2 may also represent an onium radical of formula

$-XP(O)(O^-)OCH_2CH_2N^+(CH_3)_3$

where X represents an oxygen atom or a radical $-NR_{14}$, R_{14} representing a hydrogen, a C_1-C_4 alkyl radical or a hydroxyalkyl radical.

In the context of the invention, R_2 may also represent a guanidine radical of formula $-X-C=NR_8-NR_9R_{10}$, X represents an oxygen atom or a radical $-NR_{11}$, R_8, R_9, R_{10} and R_{11} representing a hydrogen, a C_1-C_4 alkyl radical or a hydroxyalkyl radical. According to a particular embodiment, X is $-NR_{11}$, R_8 is a hydrogen, R_9 and R_{10} are chosen from hydrogen or an alkyl, preferably methyl, radical.

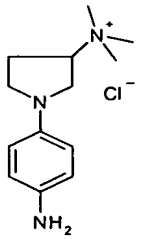
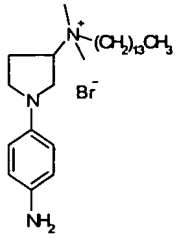
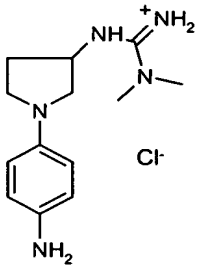
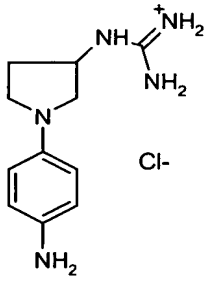
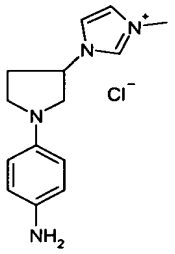
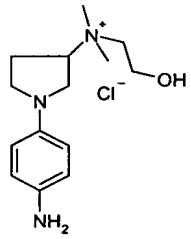
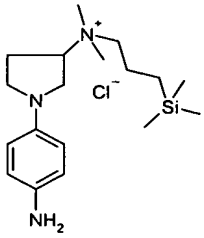
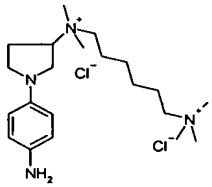
The pKa of the guanidine radical R_2 is in general such that this substituent is present in cationic form ($=NR_8H^+$) under conventional conditions for oxidation hair dyeing.

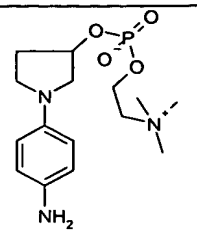
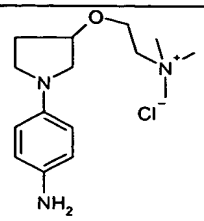
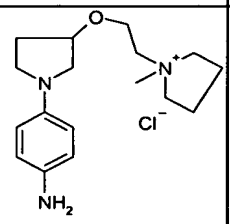
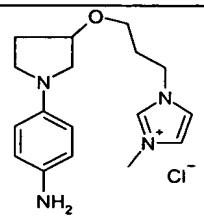
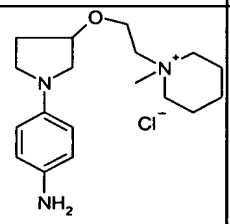
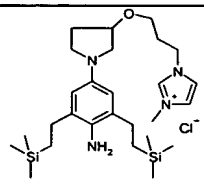
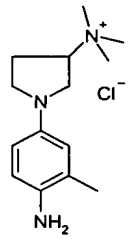
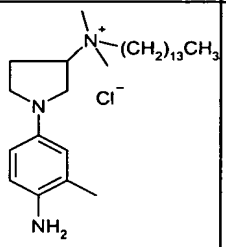
In the context of the invention, the counter-ion may be derived from a halogen atom such as bromine, chlorine, fluorine or iodine, a hydroxide, a citrate, a succinate, a tartrate, a lactate, a tosylate, a mesylate, a benzenesulphonate, an acetate, a hydrogen sulphate or a

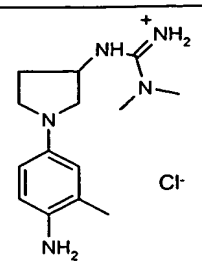
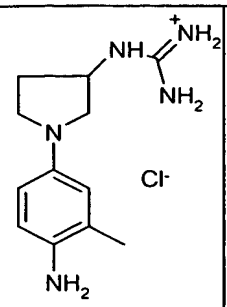
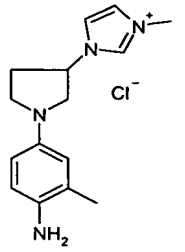
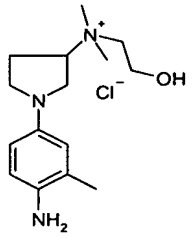
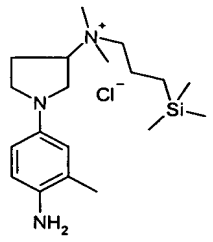
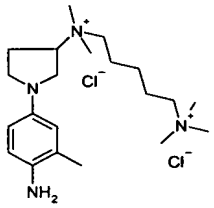
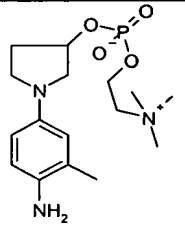
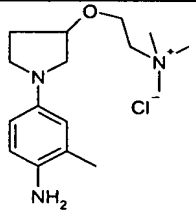
C_1-C_6 alkyl sulphate such as for example methyl sulphate or ethyl sulphate.

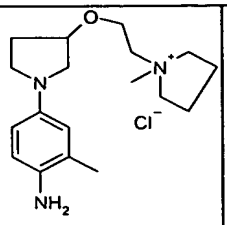
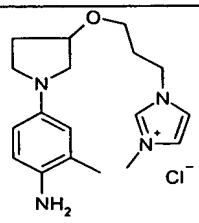
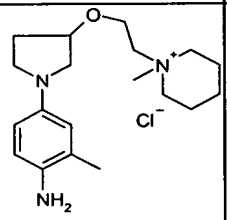
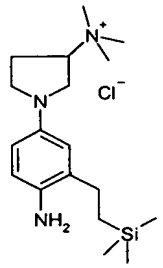
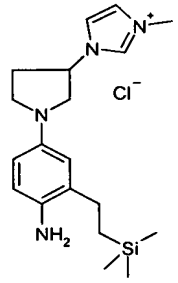
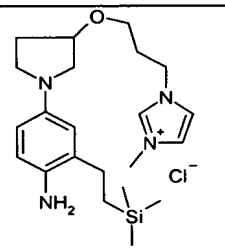
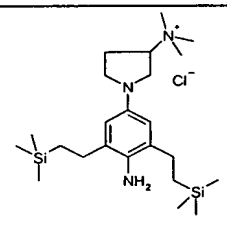
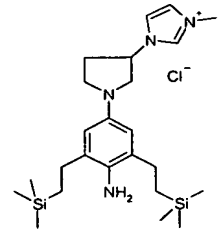
In the context of the present application, cationic tertiary para-phenylenediamines containing a pyrrolidine ring, which are described above and for which R_2 is of formula II or III, are preferably used. Still more preferably, the cationic tertiary para-phenylenediamines containing a pyrrolidine ring, which are described above and for which R_2 is of formula II or of formula III, with x=0 and for which n=0, are used.

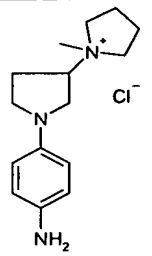
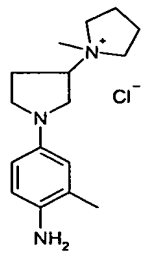
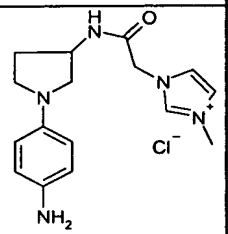
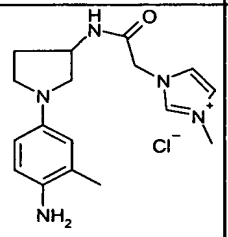
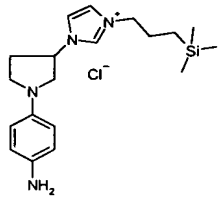
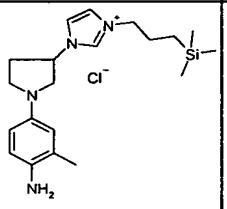
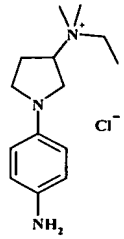
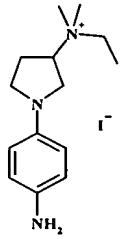
By way of example of derivatives of formula (I), there may be mentioned:

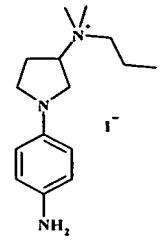
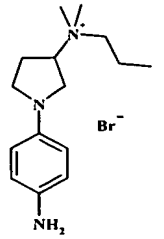
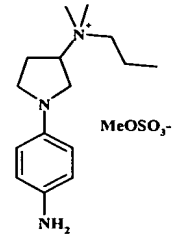
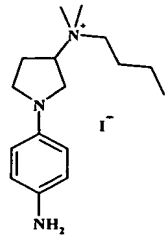
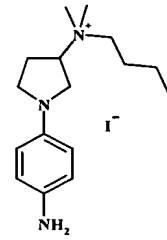
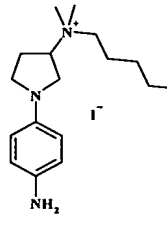
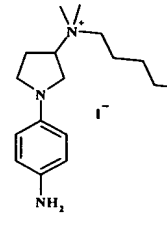
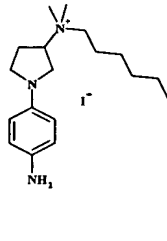
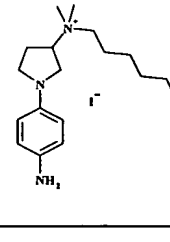
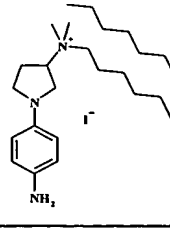
Formula	Nomenclature	Formula	Nomenclature
	[1-(4-Aminophenyl) pyrrolidin-3-yl-trimethyl-ammonium chloride (1)		[1-(4-Aminophenyl)p yrrolidin-3-yl]dimethyltetra decyl-ammonium bromide (2)
	N'-[1-(4-Aminophenyl) pyrrolidin-3-yl]-N,N-dimethyl guanidinium chloride (3)		N-[1-(4-Aminophenyl)-pyrrolidin-3-yl]guanidinium chloride (4)
	3-[1-(4-Aminophenyl) pyrrolidin-3-yl]-1-methyl-3H-imidazole-1-ium chloride (5)		[1-(4-Aminophenyl)p yrrolidin-3-yl]-(2-hydroxy-ethyl)dimethyl-ammonium chloride (6)
	[1-(4-Aminophenyl) pyrrolidin-3-yl]dimethyl-(3-trimethylsilanylpropyl)amm onium chloride (7)		[1-(4-Aminophenyl)p yrrolidin-3-yl]-(trimethyl-ammoniumhexyl)dimethyl-ammonium dichloride (8)

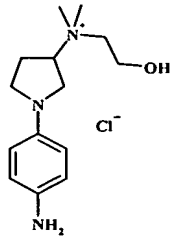
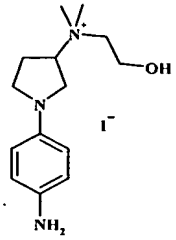
	[1-(4-Aminophenyl)-pyrrolidin-3-yl]oxophosphoryl choline (9)		{2-[1-(4-Aminophenyl)-pyrrolidin-3-yloxy]-ethyl}-trimethyl-ammonium chloride (10)
	1-{2-[1-(4-Aminophenyl) pyrrolidin-3-yloxy]ethyl}-1-methyl-pyrrolidinium ; chloride (11)		3-{3-[1-(4-Aminophenyl)pyrrolidin-3-yloxy]-propyl}-1-methyl-3H-imidazol-1-ium ; chloride (12)
	1-{2-[1-(4-Aminophenyl) pyrrolidin-3-yloxy]ethyl}-1-methyl piperidinium; chloride (13)		3-{3-[1-(5-trimethylsilanyl ethyl-4-Amino-3-trimethylsilanyl ethylphenyl)-pyrrolidin-3-yloxy]propyl}-1-methyl-3H-imidazole-1-um ; chloride (14)
	[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]-trimethylammoniumchloride (15)		[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-yl]dimethyl-tetradecyl-ammonium chloride (16)

	N'-[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-yl]-N,N-dimethyl guanidinium chloride (17)		N-[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-yl]-guanidinium chloride (18)
	3-[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-yl]-1-methyl-3H-imidazole-1-ium chloride (19)		[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-yl]-(2-hydroxyethyl)-dimethyl-ammonium chloride (20)
	[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]-dimethyl(3-trimethylsilanyl-propylammonium chloride (21)		[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-yl]-(trimethyl-ammonium-hexyl)dimethyl-ammonium dichloride (22)
	[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-yl]-oxophosphorylcholine (23)		{2-[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-yloxy]ethyl}-trimethyl-ammonium chloride (24)

	1-{2-[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yloxy]ethyl}-1-methyl-pyrrolidinium chloride (25)		3-{3-[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-yloxy]propyl}-1-methyl-3H-imidazole-1-um chloride (26)
	1-{2-[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yloxy]ethyl}-1-methylpiperidinium chloride (27)		[1-(4-Amino-3-trimethylsilanylethylphenyl)-pyrrolidin-3-yl]-trimethyl-ammonium chloride (28)
	3-[1-(4-Amino-3-trimethylsilanylethyl-phenyl)pyrrolidin-3-yl]-1-methyl-3H-imidazole-1-ium chloride (29)		3-{3-[1-(4-Amino-3-trimethylsilanylethylphenyl)-pyrrolidin-3-yloxy]propyl}-1-methyl-3H-imidazole-1-um chloride (30)
	[1-(5-trimethylsilanylethyl-4-Amino-3-trimethylsilanylethylphenyl)pyrrolidin-3-yl]-trimethylamm		3-[1-(5-trimethylsilanylethyl-4-Amino-3-trimethylsilanylethylphenyl)-pyrrolidin-3-yl]-1-methyl-3H-imidazole-1-

	oniumchloride (31)		ium chloride (32)
	1'-(4-Aminophenyl)-1-methyl-[1,3']bipyrrolidinyl-1-ium chloride (33)		1'-(4-Amino-3-methylphenyl)-1-methyl-[1,3']bipyrrolidinyl-1-ium chloride (34)
	3-{[1-(4-Aminophenyl)pyrrolidin-3-ylcarbamoyl]-methyl}-1-methyl-3H-imidazole-1-ium chloride (35)		3-{[1-(4-Amino-3-methylphenyl)-pyrrolidin-3-ylcarbamoyl]-methyl}-1-methyl-3H-imidazole-1-ium chloride (36)
	3-[1-(4-Aminophenyl)pyrrolidin-3-yl]-1-(3-trimethylsilanyl-propyl)-3H-imidazole-1-ium chloride (37)		3-[1-(4-Aminophenyl)pyrrolidin-3-yl]-1-(3-trimethylsilanyl-propyl)-3H-imidazole-1-ium chloride (38)
	[1-(4-Aminophenyl)pyrrolidin-3-yl]-ethyldimethyl ammonium chloride (39)		[1-(4-Aminophenyl)pyrrolidin-3-yl]-ethyldimethyl-ammonium iodide (40)

	[1-(4-aminophenyl) pyrrolidin-3-yl]-propyldimethylammonium iodide, (41)		[1-(4-Aminophenyl)pyrrolidin-3-yl]-propyldimethyl-ammonium bromide (42)
	[1-(4-Aminophenyl) pyrrolidin-3-yl]-propyldimethylammonium methosulphate (43)		[1-(4-Aminophenyl)pyrrolidin-3-yl]-butyldimethyl-ammonium iodide (44)
	[1-(4-Aminophenyl) pyrrolidin-3-yl]-pentyldimethylammonium iodide (45)		[1-(4-Aminophenyl)pyrrolidin-3-yl]-hexyldimethyl-ammonium iodide (46)
	[1-(4-Aminophenyl) pyrrolidin-3-yl]-heptyldimethyl-ammonium iodide (47)		[1-(4-Aminophenyl)pyrrolidin-3-yl]-octyldimethyl-ammonium iodide (48)
	[1-(4-Aminophenyl) pyrrolidin-3-yl]-decyldimethyl		[1-(4-amino-phenyl)pyrrolidin-3-yl]-hexadecyldimethylammonium

	ammonium iodide (49)		iodide (50)
	[1-(4-Aminophenyl) pyrrolidin-3-yl]-hydroxyethyl-dimethylammonium chloride (51)		[1-(4-aminophenyl)-pyrrolidin-3-yl]-hydroxyethyl-dimethyl-ammonium iodide (52)

The derivatives of formula I which are preferably used are:

[1-(4-Aminophenyl)pyrrolidin-3-yl]trimethylammonium chloride;

[1-(4-Aminophenyl)pyrrolidin-3-yl]dimethyltetradecyl-ammonium bromide;

N'-[1-(4-Aminophenyl)pyrrolidin-3-yl]-N,N-dimethyl guanidinium chloride

N-[1-(4-Aminophenyl)pyrrolidin-3-yl] guanidinium chloride

3-[1-(4-Aminophenyl)pyrrolidin-3-yl]-1-methyl-3H-imidazol-1-ium chloride ;

[1-(4-Aminophenyl)pyrrolidin-3-yl]-(2-hydroxyethyl)dimethyl-ammonium chloride

[1-(4-Aminophenyl)pyrrolidin-3-yl]dimethyl-(3-trimethylsilanylpropyl)ammonium chloride;

[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]trimethyl-ammonium chloride

[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]dimethyl-tetradecylammonium chloride

N'-[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]-N,N-dimethyl guanidinium chloride

N-[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl] guanidinium chloride

3-[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]-1-methyl-3H-imidazol-1-ium chloride

[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]-(2-hydroxyethyl)dimethylammonium chloride

[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]dimethyl-(3-trimethylsilanylpropylammonium chloride

1'-(4-Aminophenyl)-1-methyl-[1,3']bipyrrolidinyl-1-ium chloride

1'-(4-Amino-3-methylphenyl)-1-methyl-[1,3']bipyrrolidinyl-1-ium chloride

3-{[1-(4-Aminophenyl)pyrrolidin-3-ylcarbamoyl]methyl}-1-methyl-3H-imidazol-1-ium chloride

3-{[1-(4-Amino-3-methylphenyl)pyrrolidin-3-ylcarbamoyl]-methyl}-1-methyl-3H- imidazol-1-ium chloride

3-[1-(4-Aminophenyl)pyrrolidin-3-yl]-1-(3-trimethylsilanylpropyl)-3H-imidazol-1-ium chloride

3-[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]-1-(3-trimethylsilanylpropyl)-3H-imidazol-1-ium chloride

[1-(4-aminophenyl)pyrrolidin-3-yl]ethyldimethylammonium chloride

[1-(4-aminophenyl)pyrrolidin-3-yl]-ethyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]propyldimethylammonium iodide,

[1-(4-aminophenyl)pyrrolidin-3-yl]propyldimethylammonium bromide

[1-(4-aminophenyl)pyrrolidin-3-yl]propyldimethylammonium methosulphate

[1-(4-aminophenyl)pyrrolidin-3-yl]butyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]pentyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]hexyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]heptyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]octyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]decyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]hexadecyldimethyl-ammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]hydroxyethyldimethyl-ammonium chloride

[1-(4-aminophenyl)pyrrolidin-3-yl]hydroxyethyldimethyl-ammonium iodide.

More preferably, the following compounds will be used:

[1-(4-Aminophenyl)pyrrolidin-3-yl]trimethylammonium chloride

[1-(4-Aminophenyl)pyrrolidin-3-yl]dimethyltetradecyl-ammonium bromide

N'-[1-(4-Aminophenyl)pyrrolidin-3-yl]-N,N-dimethyl guanidinium chloride

N-[1-(4-Aminophenyl)pyrrolidin-3-yl] guanidinium chloride

3-[1-(4-Aminophenyl)pyrrolidin-3-yl]-1-methyl-3H-imidazol-1-ium chloride

[1-(4-Aminophenyl)pyrrolidin-3-yl]-(2-hydroxyethyl)dimethylammonium chloride

[1-(4-Aminophenyl)pyrrolidin-3-yl]dimethyl-(3-trimethylsilanylpropyl)ammonium chloride

[1-(4-Aminophenyl)pyrrolidin-3-yl]-(trimethylammonium-hexyl)dimethylammonium dichloride

1'-(4-Aminophenyl)-1-methyl[1,3']bipyrrolidinyl-1-ium chloride

3-[1-(4-Aminophenyl)pyrrolidin-3-yl]-1-(3-trimethylsilanyl-propyl)-3H-imidazol-1-ium chloride

3-[1-(4-Amino-3-methylphenyl)pyrrolidin-3-yl]-1-(3-trimethylsilanylpropyl)-3H-imidazol-1-ium chloride

[1-(4-aminophenyl)pyrrolidin-3-yl]ethyldimethylammonium chloride

[1-(4-aminophenyl)pyrrolidin-3-yl]ethyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]propyldimethylammonium iodide,

[1-(4-aminophenyl)pyrrolidin-3-yl]propyldimethylammonium bromide

[1-(4-aminophenyl)pyrrolidin-3-yl]propyldimethylammonium methosulphate

[1-(4-aminophenyl)pyrrolidin-3-yl]butyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]pentyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]hexyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]heptyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]octyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]decyldimethylammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]hexadecyldimethyl-ammonium iodide

[1-(4-aminophenyl)pyrrolidin-3-yl]hydroxyethyldimethyl-ammonium chloride

[1-(4-aminophenyl)pyrrolidin-3-yl]hydroxyethyldimethyl-ammonium iodide

Still more preferably, the following compounds will be used:

[1-(4-Aminophenyl)pyrrolidin-3-yl]trimethylammonium chloride

3-[1-(4-Aminophenyl)pyrrolidin-3-yl]-1-methyl-3H-imidazol-1-ium chloride

[1-(4-Aminophenyl)pyrrolidin-3-yl]-(2-hydroxyethyl)-dimethylammonium chloride

1'-(4-Aminophenyl)-1-methyl[1,3']bipyrrolidinyl-1-ium chloride, and in particular

[1-(4-Aminophenyl)pyrrolidin-3-yl]trimethylammonium chloride, and

[1-(4-Aminophenyl)pyrrolidin-3-yl]-(2-hydroxyethyl)-dimethylammonium chloride.

The counter-ion is not critical as for the result of the invention, any compounds similar to the preferred compounds described above but with a different counter-ion forms an integral part of the preferred compounds.

The cation tertiary para-phenylenediamine(s) containing a pyrrolidine ring represent from 0.001% to 10%, and preferably from

0.005% to 6% by weight relative to the total weight of the composition.

The compounds of formula (I) may be synthesized according to known methods, and in particular methods described in application WO 02/45675.

The polymers containing a fatty chain, also called "associative polymers", possess at least one linear or branched, saturated or unsaturated, C_8-C_{30}, preferentially C_{10}-C_{24} and preferably C_{12}-C_{18} hydrocarbon chain.

The polymers containing a fatty chain which can be used in the compositions according to the present application are chosen from cationic polymers containing a fatty chain (that is to say cationic associative polymers) such as polyurethanes, celluloses, or derivatives of polyvinylpyrrolidone or anionic polymers containing a fatty chain (that is to say anionic associative polymers) such as polymers containing the units (C_{10}-C_{30})alkyl esters of (meth)acrylic acid or allyl ethers containing a fatty chain.

As cationic polymers containing a fatty chain, the cationic associative polyurethanes described in French patent application No. 00 09609 of (Va) may be used of formula (Va):

$$R\text{-}X\text{-}(P)_n\text{-}[L\text{-}(Y)_m]_r\text{-}L'\text{-}(P')_p\text{-}X'\text{-}R' \qquad (Va)$$

in which:

R and R', which are identical or different, represent a hydrophobic group or a hydrogen atom;

X and X', which are identical or different, represent a group containing an amine functional group carrying or otherwise a hydrophobic group, or alternatively the group L";

L, L' and L", which are identical or different, represent a group derived from a diisocyanate;

P and P', which are identical or different, represent a group containing an amine functional group carrying or otherwise a hydrophobic group;

Y represents a hydrophilic group;

r is an integer between 1 and 100, preferably between 1 and 50 and in particular between 1 and 25;

n, m and p are each, independently of the others, between 0 and 1000;

the molecule containing at least one protonated or quaternized amine functional group and at least one hydrophobic group.

In a preferred embodiment of the polyurethanes of the present invention, the only hydrophobic groups are the groups R and R' at the chain ends.

A preferred family of cationic associative polyurethanes is that corresponding to the formula (Va) described above and in which:

R and R' both represent independently a hydrophobic group,

X, X' each represent a group L",

n and p are between 1 and 1000, and

L, L', L", P, P', Y and m have the meaning indicated above.

Another preferred family of cationic associative polyurethanes is that corresponding to the formula (Va) above in which:

R and R' both represent independently a hydrophobic group, X, X' each represent a group L", n and p are equal to 0, and L, L', L", Y and m have the meaning indicated above.

The fact that n and p are equal to 0 means that these polymers do not contain units derived from a monomer containing an amine functional group, incorporated into the polymer during polycondensation. The protonated amine functional groups of these polyurethanes result from the hydrolysis of isocyanate functional groups, in excess, at the chain end, followed by alkylation of the primary amine functional groups formed by alkylating agents containing a hydrophobic group, that is to say compounds of the RQ or R'Q type, in which R and R' are as defined above and Q denotes a leaving group such as a halide, a sulphate and the like.

Yet another preferred family of cationic associative polyurethanes is that corresponding to the formula (Va) above in which:

R and R' both represent independently a hydrophobic group,

X and X' both represent independently a group containing a quaternary amine,

n and p are equal to zero, and

L, L', Y and m have the meaning indicated above.

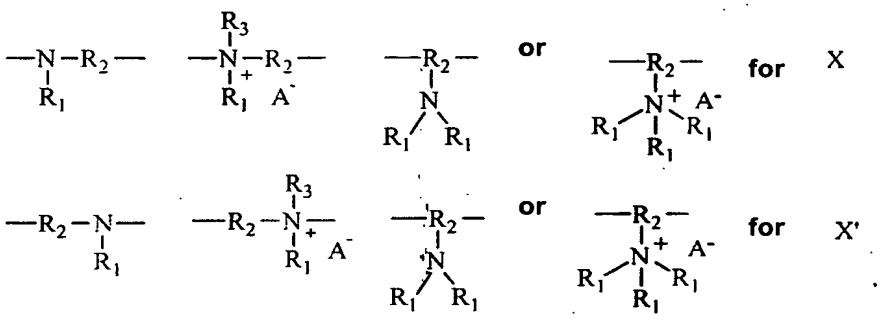
The number-average molecular mass of the cationic associative polyurethanes is preferably between 400 and 500 000, in particular between 1 000 and 400 000, and ideally between 1 000 and 300 000.

The expression hydrophobic group is understood to mean a radical or polymer containing a saturated or unsaturated, linear or branched hydrocarbon chain which may contain one or more heteroatoms such as P, O, N, S or a radical containing a perfluorinated or silicone chain. When it denotes a hydrocarbon radical, the hydrophobic group contains at least 10 carbon atoms, preferably from 10 to 30 carbon atoms, in particular from 12 to 30 carbon atoms, and more preferably from 18 to 30 carbon atoms.

Preferably, the hydrocarbon group is derived from a monofunctional compound.

By way of example, the hydrophobic group may be derived from a fatty alcohol such as stearyl alcohol, dodecyl alcohol, decyl alcohol. It may also denote a hydrocarbon polymer such as for example polybutadiene.

When X and/or X' denote a group containing a tertiary or quaternary amine, X and/or X' may represent one of the following formulae:



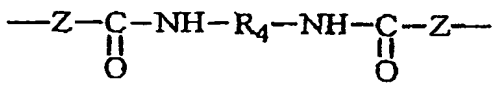
in which:

R_2 represents a linear or branched alkylene radical having from 1 to 20 carbon atoms, containing or otherwise a saturated or unsaturated ring, or an arylene radical, it being possible for one or more of the carbon atoms to be replaced by a heteroatom chosen from N, S, O, P;

R_1 and R_3, which are identical or different, denote a linear or branched C_1-C_{30} alkyl or alkenyl radical, an aryl radical, it being possible for at least one of the carbon atoms to be replaced by a heteroatom chosen from N, S, O, P;

A^- is a physiologically acceptable counter-ion.

The groups L, L' and L" represent a group of formula:



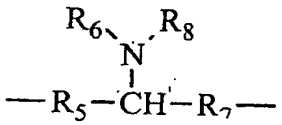
in which:

Z represents -O-, -S- or -NH-; and

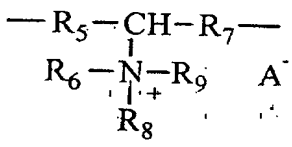
R_4 represents a linear or branched alkylene radical having from 1 to 20 carbon atoms, containing or otherwise a saturated or unsaturated ring, an arylene radical, it being possible for one or more of the carbon atoms to be replaced by a heteroatom chosen from N, S, O and P.

The groups P and P', comprising an amine functional group, may represent at least one of the following formulae:

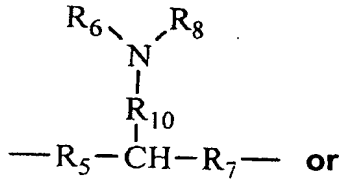
or



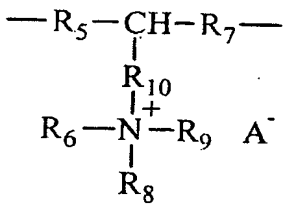
or



or



or



in which:

R_5 and R_7 have the same meanings as R_2 defined above;

R_6, R_8 and R_9 have the same meanings as R_1 and R_3 defined above;

R_{10} represents a linear or branched alkylene group, which is optionally unsaturated and which may contain one or more heteroatoms chosen from N, O, S and P,

and A^- is a physiologically acceptable counter-ion.

As regards the meaning of Y, the expression hydrophilic group is understood to mean a polymeric or nonpolymeric water-soluble group.

By way of example, there may be mentioned, when polymers are not involved, ethylene glycol, diethylene glycol and propylene glycol.

In the case, in accordance with a preferred embodiment of the invention, of a hydrophilic polymer, there may be mentioned, by way of example, polyethers, sulphonated polyesters, sulphonated polyamides, or a mixture of these polymers. Preferably, the hydrophilic compound is a polyether and in particular a polyethylene oxide or a polypropylene oxide.

The cationic associative polyurethanes of formula (Va) which can be used according to the invention are formed from diisocyanates and from various compounds possessing functional groups containing a labile hydrogen. The functional groups containing a labile hydrogen may be alcohol functional groups, primary or secondary amine functional groups or thiol functional groups which give, after reaction with the diisocyanate functional groups, polyurethanes, polyureas and polythioureas, respectively. The term "polyurethanes" of the present invention covers these three types of polymer, namely polyurethanes proper, polyureas and polythioureas and copolymers thereof.

A first type of compounds entering into the preparation of the polyurethane of formula (Va) is a compound containing at least one unit containing an amine functional group. This compound may be multifunctional, but preferably the compound is difunctional, that is to say that according to a preferred embodiment, this compound contains two labile hydrogen atoms carried for example by a hydroxyl, primary amine, secondary amine or thiol functional group. It is also possible to use a mixture of multifunctional and difunctional compounds in which the percentage of multifunctional compounds is low.

As indicated above, this compound may contain more than one unit containing an amine functional group. It is then a polymer carrying a repeat of the unit containing an amine functional group.

This type of compounds may be represented by one of the following formulae:

$HZ\text{-}(P)_n\text{-}ZH$,

or

$HZ\text{-}(P')_p\text{-}ZH$,

in which Z, P, P', n and p are as defined above.

By way of example of a compound containing an amine functional group, there may be mentioned N-methyldiethanolamine, N-tert-butyldiethanolamine, N-sulphoethyldiethanolamine.

The second compound entering into the preparation of the polyurethane of formula (Va) is a diisocyanate corresponding to the formula:

$O=C=N\text{-}R_4\text{-}N=C=O$

in which R_4 is defined above.

By way of example, there may be mentioned methylenediphenyl diisocyanate, methylenecyclohexane diisocyanate, isophorone diisocyanate, toluene diisocyanate, naphthalene diisocyanate, butane diisocyanate, hexane diisocyanate.

A third compound entering into the preparation of the polyurethane of formula (Va) is a hydrophobic compound intended to form the terminal hydrophobic groups of the polymer of formula (Va).

This compound consists of a hydrophobic group and a functional group containing a labile hydrogen, for example a hydroxyl, primary or secondary amine, or thiol functional group.

By way of example, this compound may be a fatty alcohol, such as in particular stearyl alcohol, dodecyl alcohol, decyl alcohol. When this compound contains a polymeric chain, it may be for example hydroxyl-hydrogenated polybutadiene.

The hydrophobic group of the polyurethane of formula (Va) may also result from the quaternization reaction of the tertiary amine of the compound containing at least one tertiary amine unit. Thus, the hydrophobic group is introduced by the quaternizing agent. This quaternizing agent is a compound of the RQ or R'Q type, in which R and R' are as defined above and Q denotes a leaving group such as a halide, a sulphate, and the like.

The cationic associative polyurethane may additionally comprise a hydrophilic sequence. This sequence is provided by a fourth type of compound entering into the preparation of the polymer.

This compound may be multifunctional. It is preferably difunctional. It is also possible to have a mixture where the percentage of multifunctional compound is low.

The functional groups containing a labile hydrogen are alcohol, primary or secondary amine, or thiol functional groups. This compound may be a polymer terminated at the chain ends by one of these functional groups containing a labile hydrogen.

By way of example, there may be mentioned, when polymers are not involved, ethylene glycol, diethylene glycol and propylene glycol.

In the case of a hydrophilic polymer, there may be mentioned, by way of example, polyethers, sulphonated polyesters, sulphonated polyamides, or a mixture of these polymers. Preferably, the hydrophilic compound is a polyether and in particular a polyethylene oxide or a polypropylene oxide.

The hydrophilic group noted Y in formula (Va) is optional. Indeed, the units containing a quaternary or protonated amine functional group may suffice to provide the solubility or water-dispersibility necessary for this type of polymer in an aqueous solution.

Although the presence of a hydrophilic group Y is optional, cationic associative polyurethanes are nevertheless preferred which contain such a group.

The said cationic associative polyurethanes are water-soluble or water-dispersible.

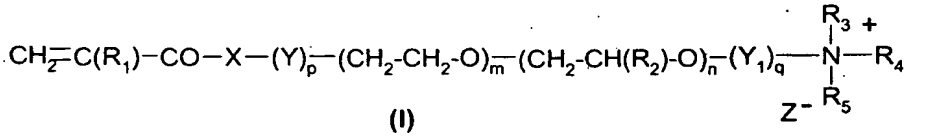
As cationic polymers containing a fatty chain, it is also possible to use cationic celluloses containing a fatty chain and more particularly the quaternized celluloses modified by groups comprising at least one fatty chain, chosen from alkyl, arylalkyl or alkylaryl groups comprising from 8 to 30 carbon atoms, or mixtures thereof.

There may be mentioned as examples of quaternized alkylhydroxyethylcelluloses containing C_8-C_{30} fatty chains the products QUATRISOFT LM 200®, QUATRISOFT LM-X 529-18-A®, QUATRISOFT LM-X 529-18B® (C_{12} alkyl) and QUATRISOFT LM-X 529-8® (C_{18} alkyl) marketed by the company AMERCHOL and the products CRODACEL QM®, CRODACEL QL® (C_{12} alkyl) and CRODACEL QS® (C_{18} alkyl) marketed by the company CRODA.

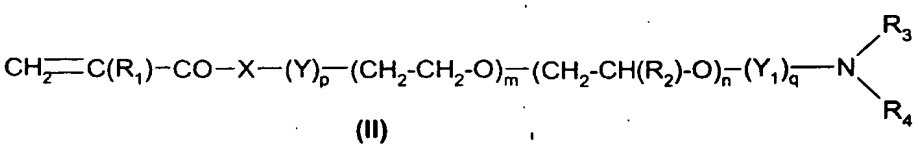
As cationic polymers containing the fatty chain, it is also possible to use the cationic derivatives of polyvinylpyrrolidone (PVP) containing a fatty chain and in particular cationic derivatives of PVP containing a fatty chain comprising

1) at least one cationic monomer of the vinylpyrrolidone type containing a fatty chain

2) at least one monomer having the following structure (I) or (II):



(I)



(II)

in which:

X denotes an oxygen atom or a radical NR_6,

R_1 and R_6 denote, independently of each other, a hydrogen atom or a linear or branched C_1-C_5 alkyl radical,

R_2 denotes a linear or branched C_1-C_4 alkyl radical,

R_3, R_4 and R_5 denote, independently of each other, a hydrogen atom, a linear or branched C_1-C_{30} alkyl radical or a radical of formula (III):

$$-(Y_2)_r-(CH_2\text{-}CH(R_7)\text{-}O)_x-R_8 \qquad (III)$$

Y, Y_1 and Y_2 denote, independently of each other, a linear or branched C_2-C_{16} alkylene radical,

R_7 denotes a hydrogen atom, or a linear or branched C_1-C_4 alkyl radical or a linear or branched C_1-C_4 hydroxyalkyl radical,

R_8 denotes a hydrogen atom or a linear or branched C_1-C_{30} alkyl radical,

p, q and r denote, independently of each other, either the value zero, or the value 1,

m and n denote, independently of each other, an integer ranging from 0 to 100,

x denotes an integer ranging from 1 to 100,

Z denotes an anion of an organic or inorganic acid,

provided that:

- at least one of the substituents R_3, R_4, R_5 or R_8 denotes a linear or branched C_9-C_{30} alkyl radical,
- if m or n is different from zero, then q is equal to 1,
- if m or n are equal to zero, then p or q is equal to 0.

Preferably, the counter ion Z^- of the monomers of formula (I) is chosen from the halide ions, the phosphate ions, the methosulphate ion, the tosylate ion.

Preferably, R_3, R_4 and R_5 denote, independently of each other, a hydrogen atom or a linear C_1-C_{30} alkyl radical.

More preferably, the monomer b) is a monomer of formula (I) for which, still more preferably, m and n are equal to zero.

The cationic PVPs containing a fatty chain may also contain one or more additional cationic or nonionic monomers. Among the latter, there may be mentioned C_1-C_6 alkyl acrylates and methacrylates.

As cationic PVPs containing a fatty chain which are particularly preferred, there may be mentioned the terpolymers comprising

a) - a monomer of the pyrrolidone type,

b) - a monomer of formula (I) in which p = 1, q = 0, R_3 and R_4 denote, independently of each other, a hydrogen atom or a C_1-C_5 alkyl radical and R_5 denotes a C_9-C_{24} alkyl radical, and

c) - a monomer of formula (II) in which R_3 and R_4 denote, independently of each other, a hydrogen atom or a C_1-C_5 alkyl radical.

Still more particularly, the terpolymers comprising, by weight, 40 to 95% of monomer (a), 0.25 to 50% of monomer (b) and 0.1 to 55% of monomer (c) are used.

They are for example the terpolymers vinylpyrrolidone/dimethylaminopropylmethacrylamide/dodecyldimethylmethacrylamidopropylammonium tosylate, the terpolymers vinylpyrrolidone/dimethylaminopropylmethacrylamide/cocoyldimethylmethacrylamidopropylammonium tosylate, the terpolymers vinylpyrrolidone/dimethylaminopropylmethacrylamide/lauryldimethylmethacrylamidopropylammonium tosylate or chloride.

The weight-ratio molecular mass of the cationic polyvinylpyrrolidones is between 500 and 20 000 000, preferably

between 200 000 and 2 000 000 and more preferably between 400 000 and 800 000.

As cationic polyvinylpyrrolidone which can be used according to the invention, there may be mentioned the product ACP 1234 from ISP.

As anionic polymer containing a fatty chain, it is possible to use an anionic amphiphilic polymer containing at least one hydrophilic unit chosen from the units acrylic acid and methacrylic acid and at least one hydrophobic unit chosen from the units of the (C_{10}-C_{30})alkyl ester of acrylic acid type and of the (C_{10}-C_{30})alkyl ester of methacrylic acid type.

Preferably, the hydrophobic unit of the anionic amphiphilic polymer is chosen from the units of the (C_{12}-C_{22})alkyl ester of acrylic acid type and of the (C_{12}-C_{22})alkyl ester of methacrylic acid type.

It is in particular a polymer of acrylic acid and of lauryl methacrylate.

As a polymer of this family, there may be mentioned the polymers PEMULEN TR1 and TR2 and CARBOPOL 1382 from GOODRICH, and the polymer COATEX SX from SEPPIC.

The passage of application EP 0 827 738 relating to these anionic amphiphilic polymers and to their synthesis is incorporated by reference into the present application.

As anionic polymer containing a fatty chain, it is also possible to use an anionic polymer containing a fatty chain and an anionic amphiphilic polymer containing at least one hydrophilic unit of the acrylic acid type and at least one allyl ether unit containing a fatty chain.

Preferably, the allyl ether unit containing a fatty chain corresponds to the monomer having the following formula (I):

$$CH_2 = C\ R'\ CH_2\ O\ B_n\ R \qquad (I)$$

in which R' denotes H or CH_3, B denotes the ethyleneoxy radical, n is zero or denotes an integer ranging from 1 to 100, R denotes a hydrocarbon radical chosen from the alkyl, arylalkyl, aryl, alkylaryl or cycloalkyl radicals, comprising from 8 to 30 carbon atoms, preferably 10 to 24, and more particularly from 12 to 18 carbon atoms.

These anionic amphiphilic polymers can be prepared by a method of polymerization in emulsion described in patent EP-0 216 479 B2.

A more particularly preferred unit of formula (I) is a unit in which R' denotes H, n is equal to 10 and R denotes a stearyl radical (C_{18}).

Among these anionic amphipilic polymers, the polymers formed from 20 to 60% by weight of acrylic acid and/or of methacrylic acid, from 5 to 60% by weight of lower alkyl (meth)acrylates, from 2 to 50% by weight of allyl ether containing a fatty chain of formula (XV), and from 0 to 1% by weight of a crosslinking agent which is a well-known copolymerizable polyethylenic unsaturated monomer such as diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate and methylenebisacrylamide, are particularly used.

In the compositions according to the present invention, the polymer containing a fatty chain represents from 0.05% to 20%, preferentially from 0.1% to 10% and preferably from 0.5% to 5% by weight relative to the total weight of the composition.

According to a first preferred embodiment, the composition according to the present invention additionally contains at least one additional cationic polymer.

For the purposes of the present invention, the expression additional "cationic polymer" denotes any polymer containing cationic groups and/or groups which are ionizable to cationic groups other than the polymers containing a fatty chain which are useful in the composition according to the present application.

The cationic polymers which can be used in accordance with the present invention may be chosen from all those already known per se as improving the cosmetic properties of hair, namely in particular those described in patent application EP-A-337 354 and in French patents FR-2 270 846, 2 383 660, 2 598 611, 2 470 596 and 2 519 863.

The preferred additional cationic polymers are chosen from those which contain units comprising primary, secondary, tertiary and/or quaternary amine groups which may either be part of the main polymer chain, or which may be carried by a side substituent directly linked to the latter.

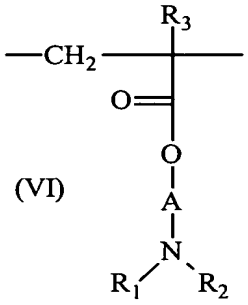
The additional cationic polymers used generally have a number-average molecular mass between 500 and 5.10^6 approximately, and preferably between 10^3 and 3.10^6 approximately.

Among the additional cationic polymers, there may be mentioned more particularly polymers of the polyamine, polyamino amide and poly(quaternaryammonium) type.

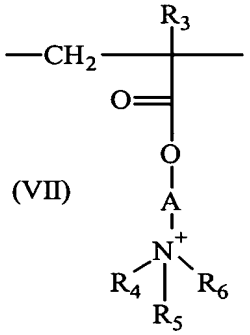
They are known products. They are described in particular in French patents No. 2 505 348 or 2 542 997. Among the said polymers, there may be mentioned:

the homopolymers or copolymers derived from acrylic or methacrylic esters or amides and comprising at least one of the units of the following formulae (VI), (VII), (VIII) or (IX):

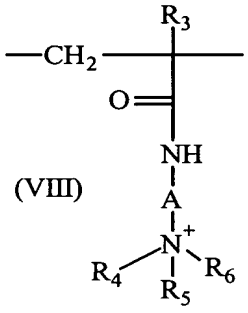
(VI)



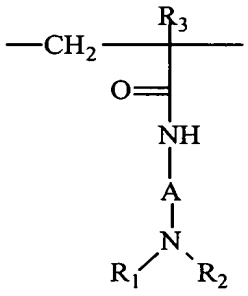
(VII)



(VIII)



(IX)



in which:

R_3 denotes a hydrogen atom or a CH_3 radical;

A represents a linear or branched alkyl group of 1 to 6 carbon atoms, preferably 2 or 3 carbon atoms or a hydroxyalkyl group of 1 to 4 carbon atoms;

R_4, R_5, R_6, which are identical or different, represent an alkyl group having from 1 to 6 carbon atoms;

R_1 and R_2, which are identical or different, represent hydrogen or an alkyl group having from 1 to 6 carbon atoms and preferably methyl or ethyl;

X^- denotes an anion derived from an inorganic or organic acid such as a methosulphate anion or a halide such as chloride or bromide.

The polymers of the family (1) may contain, in addition, one or more units derived from comonomers which may be chosen from the family of acrylamides, methacrylamides, diacetone acrylamides, acrylamides and methacrylamides substituted on the nitrogen with lower (C_1-C_4)alkyls, acrylic or methacrylic acids or esters thereof, vinyllactams such as vinylpyrrolidone or vinylcaprolactam, vinyl esters.

Thus, among these polymers of the family (1), there may be mentioned:

- the copolymers of acrylamide and dimethylaminoethyl methacrylate quaternized with dimethyl sulphate or with a dimethyl halide such as that sold under the name HERCOFLOC by the company HERCULES,
- the copolymers of acrylamide and methacryloyloxyethyltrimethylammonium chloride described, for example, in Patent Application EP-A-080976 and sold under the name BINA QUAT P 100 by the company CIBA GEIGY,
- the copolymer of acrylamide and methacryloyloxyethyltrimethylammonium methosulphate sold under the name RETEN by the company HERCULES,
- the vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers, quaternized or otherwise, such as the products sold under the name "GAFQUAT" by the company ISP such as for example "GAFQUAT 734" or "GAFQUAT 755" or alternatively the products called "COPOLYMER 845, 958 and 937". These polymers are described in detail in French Patents 2 077 143 and 2 393 573,
- the dimethylaminoethyl methacrylate/vinylcaprolactam/vinylpyrrolidone terpolymers such as the product sold under the name GAFFIX VC 713 by the company ISP,
- the vinylpyrrolidone/methacrylamidopropyldimethylamine copolymers marketed in particular under the name STYLEZE CC 10 by ISP,

- and the quaternized vinylpyrrolidone/dimethyl aminopropyl methacrylamide copolymers such as the product sold under the name "GAFQUAT HS 100" by the company ISP.

(2) The cellulose ether derivatives comprising quaternary ammonium groups, described in French Patent 1 492 597, and in particular the polymers marketed under the names "JR" (JR 400, JR 125, JR 30M) or "LR" (LR 400, LR 30M) by the company Union Carbide Corporation. These polymers are also defined in the CTFA dictionary as hydroxyethyl cellulose quaternary ammoniums which have reacted with an epoxide substituted by a trimethylammonium group.

(3) Cationic cellulose derivatives such as cellulose copolymers or cellulose derivatives grafted with a quaternary ammonium water-soluble monomer, and described especially in US Patent 4 131 576, such as hydroxyalkyl celluloses like hydroxymethyl, hydroxyethyl or hydroxypropyl celluloses grafted especially with a methacryloylethyltrimethylammonium, methacrylamidopropyl-trimethylammonium or dimethyldiallylammonium salt.

The commercialized products corresponding to this definition are more particularly the products sold under the name "Celquat L 200" and "Celquat H 100" by the company National Starch.

(4) The cationic polysaccharides described more particularly in US Patents 3 589 578 and 4 031 307 such as guar gums containing cationic trialkylammonium groups. Guar gums modified with a 2,3-epoxypropyltri methylammonium salt (e.g. chloride) are for example used.

Such products are marketed in particular under the trade names JAGUAR C13 S, JAGUAR C 15, JAGUAR C 17 or JAGUAR C162 by the company MEYHALL.

(5) Polymers consisting of piperazinyl units and of alkylene or hydroxyalkylene divalent radicals with straight or branched chains, optionally interrupted by oxygen, sulphur or nitrogen atoms or by aromatic or heterocyclic rings, as well as the oxidation and/or quaternization products of these polymers. Such polymers are described especially in French patents 2 162 025 and 2 280 361;

(6) Water-soluble polyaminoamides prepared in particular by polycondensation of an acid compound with a polyamine; these polyaminoamides may be crosslinked with an epihalohydrin, a

diepoxide, a dianhydride, an unsaturated dianhydride, a diunsaturated derivative, a bishalohydrin, a bisazetidinium, a bishaloacyldiamine, an alkylbishalide or else with an oligomer resulting from the reaction of a difunctional compound which is reactive towards a bishalohydrin, a bisazetidinium, a bishaloacyldiamine, an alkylbishalide, an epihalohydrin, a diepoxide or a diunsaturated derivative; the crosslinking agent being employed in proportions ranging from 0.025 to 0.35 mol per amine group of the polyaminoamide; these polyaminoamides may be alkylated or, if they include one or more tertiary amine functional groups, quaternized. Such polymers are described especially in French Patents 2 252 840 and 2 368 508.

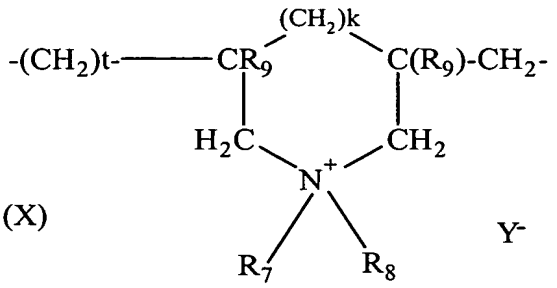
(7) Polyaminoamide derivatives resulting from the condensation of polyalkylenepolyamines with polycarboxylic acids, followed by an alkylation with difunctional agents. There may be mentioned, for example, the adipic acid/dialkylaminohydroxyalkyldialkylenetriamine polymers in which the alkyl radical contains from 1 to 4 carbon atoms and preferably denotes methyl, ethyl or propyl. Such polymers are described especially in French Patent 1 583 363.

Among these derivatives there may be mentioned more particularly the adipic acid/dimethyl aminohydroxypropyl/diethylenetriamine polymers sold under the name "Cartaretine F, F4 or F8" by the company Sandoz.

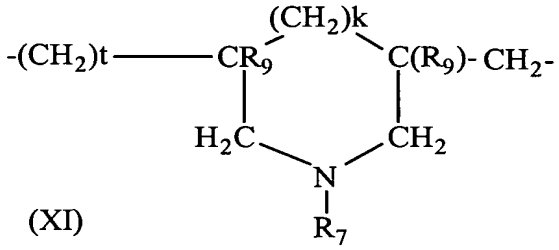
(8) Polymers obtained by reaction of a polyalkylenepolyamine containing two primary amine groups and at least one secondary amine group with a dicarboxylic acid chosen from diglycolic acid and saturated aliphatic dicarboxylic acids containing from 3 to 8 carbon atoms. The molar ratio of the polyalkylenepolyamine to the dicarboxylic acid being between 0.8 : 1 and 1.4 : 1; the polyaminoamide resulting therefrom being made to react with epichlorohydrin in a molar ratio of epichlorohydrin relative to the secondary amine group of the polyaminoamide of between 0.5 : 1 and 1.8 : 1. Such polymers are described especially in American Patents 3 227 615 and 2 961 347.

Polymers of this type are marketed in particular under the name "Hercosett 57" by the company Hercules Inc. or else under the name of "PD 170" or "Delsette 101" by the company Hercules in the case of the copolymer of adipic acid/epoxypropyl/diethylene triamine.

(9) Cyclopolymers of alkyldiallylamine or of dialkyldiallylammonium, such as the homopolymers or copolymers comprising, as main constituent of the chain, units corresponding to the formulae (X) or (XI):



(X)



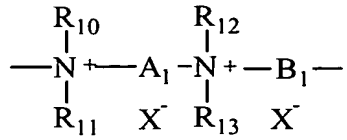
(XI)

in which formulae k and t are equal to 0 or 1, the sum k + t being equal to 1; R_9 denotes a hydrogen atom or a methyl radical; R_7 and R_8, independently of each other, denote an alkyl group containing from 1 to 6 carbon atoms, a hydroxyalkyl group in which the alkyl group preferably has 1 to 5 carbon atoms, or a lower (C_1-C_4)amidoalkyl group or R_7 and R_8 may denote, jointly with the nitrogen atom to which they are attached, heterocyclic groups such as piperidinyl or morpholinyl; R_7 and R_8, independently of each other, preferably denote an alkyl group having 1 to 4 carbon atoms; Y- is an anion such as bromide, chloride, acetate, borate, citrate, tartrate, bisulphate, bisulphite, sulphate or phosphate. These polymers are described especially in French Patent 2 080 759 and in its certificate of addition 2 190 406.

Among the polymers defined above there may be mentioned more particularly the dimethyldiallylammonium chloride homopolymer sold under the name "Merquat 100" by the company Calgon (and its homologues of low weight-average molecular masses) and the

copolymers of diallyl dimethylammonium chloride and acrylamide marketed under the name "MERQUAT 550".

(10) The quaternary diammonium polymer containing repeat units corresponding to the formula:



(XII)

formula (XII) in which:

R_{10}, R_{11}, R_{12} and R_{13}, which are identical or different, represent aliphatic, alicyclic or arylaliphatic radicals containing from 1 to 6 carbon atoms or lower hydroxyalkyl aliphatic radicals, or else R_{10}, R_{11}, R_{12} and R_{13}, together or separately, form, with the nitrogen atoms to which they are attached, heterocyclic rings optionally containing a second heteroatom other than nitrogen, or else R_{10}, R_{11}, R_{12} and R_{13} denote a linear or branched C_1-C_6 alkyl radical substituted by a nitrile, ester, acyl, amide or -CO-O-R_{14}-D or -CO-NH-R_{14}-D group where R_{14} is an alkylene and D a quaternary ammonium group;

A_1 and B_1 represent polymethylene groups containing from 2 to 20 carbon atoms which may be linear or branched, saturated or unsaturated and which may contain, bonded to or inserted into the main chain, one or more aromatic rings, or one or more oxygen or sulphur atoms or sulphoxide, sulphone, disulphide, amino, alkylamino, hydroxyl, quaternary ammonium, ureido, amide or ester groups, and

X- denotes an anion derived from an inorganic or organic acid;

A1, R_{10} and R_{12}, with the two nitrogen atoms to which they are attached, may form a piperazine ring; in addition if A_1 denotes a saturated or unsaturated, linear or branched alkylene or hydroxyalkylene radical, B_1 may also denote a group -(CH_2)n-CO-D-OC-(CH_2)n- in which D denotes:

a) a glycol residue of formula: -O-Z-O-, where Z denotes a linear or branched hydrocarbon radical or a group corresponding to one of the following formulae:

-$(CH_2$-CH_2-O)x-CH_2-CH_2-

-[CH_2-CH(CH_3)-O]y-CH_2-CH(CH_3)-

where x and y denote an integer from 1 to 4, representing a defined and unique degree of polymerization or any number from 1 to 4 representing a mean degree of polymerization;

b) a disecondary diamine residue such as a piperazine derivative;

c) a diprimary diamine residue of formula: -NH-Y-NH-, where Y denotes a linear or branched hydrocarbon radical or else the divalent radical

$-CH_2-CH_2-S-S-CH_2-CH_2-$;

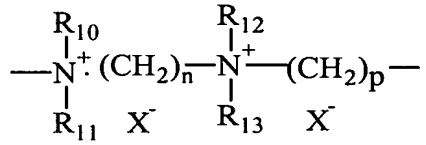
d) a ureylene group of formula: -NH-CO-NH-;

X- is preferably an anion such as chloride or bromide.

These polymers have a number-average molecular mass which is generally between 1 000 and 100 000.

Polymers of this type are described especially in French Patents 2 320 330, 2 270 846, 2 316 271, 2 336 434 and 2 413 907 and US Patents 2 273 780, 2 375 853, 2 388 614, 2 454 547, 3 206 462, 2 261 002, 2 271 378, 3 874 870, 4 001 432, 3 929 990, 3 966 904, 4 005 193, 4 025 617, 4 025 627, 4 025 653, 4 026 945 and 4 027 020.

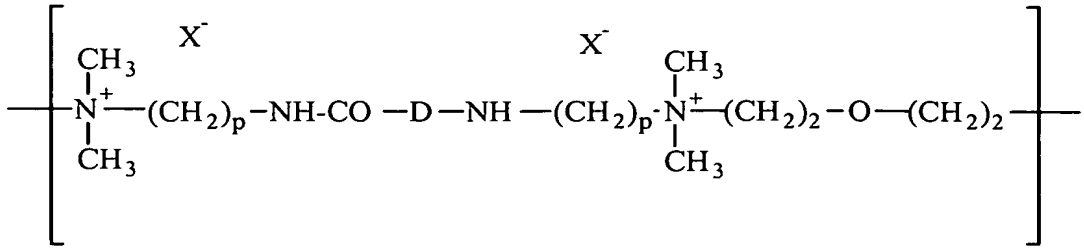
It is possible to use more particularly the polymers which consist of repeat units corresponding to the following formula (XIII):



(XIII)

in which R_{10}, R_{11}, R_{12} and R_{13}, which are identical or different, denote an alkyl or hydroxyalkyl radical having from 1 to 4 carbon atoms approximately, n and p are integers varying from 2 to 20 approximately and X- is an anion derived from an inorganic or organic acid.

(11) The quaternary polyammonium polymers consisting of repeat units of formula XIV):



(XIV)

in which p denotes an integer varying from 1 to 6 approximately, D may be zero or may represent a group $-(CH_2)_r-CO-$ in which r denotes a number equal to 4 or to 7, X- is an anion.

Such polymers may be prepared according to the methods described in USA Patents No. 4 157 388, 4 702 906, 4 719 282. They are in particular described in patent application EP-A-122 324.

Among these, there may be mentioned for example the products "Mirapol A 15", "Mirapol AD1", "Mirapol AZ1" and Mirapol 175" sold by the company Miranol.

(12) Quaternary vinylpyrrolidone and vinylimidazole polymers such as, for example, the products marketed under the names Luviquat FC 905, FC 550 and FC 370 by the company B.A.S.F.

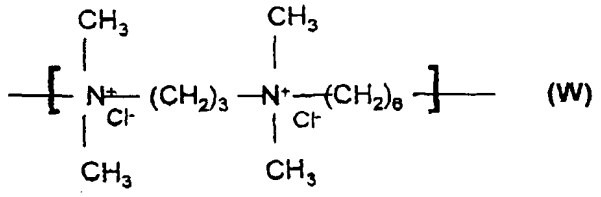
(13) Polyamines like the Polyquart H sold by HENKEL, referenced under the name of "Polyethylene glycol (15) Tallow Polyamine" in the CTFA dictionary.

(14) The crosslinked polymers of methacryloyloxy(C_1-C_4 alkyl)tri(C_1-C_4 alkyl)ammonium salts such as the polymers obtained by homopolymerization of dimethylaminoethyl methacrylate quaternized with methyl chloride, or by copolymerization of acrylamide with dimethylaminoethyl methacrylate quaternized with methyl chloride, the homo- or copolymerization being followed by crosslinking with a compound containing olefinic unsaturation, in particular methylenebisacrylamide. More particularly, it is possible to employ a crosslinked acrylamide/methacryloyloxyethyltrimethyl-ammonium chloride copolymer (20/80 by weight) in the form of a dispersion containing 50% by weight of the said copolymer in mineral oil. This dispersion is marketed under the name of "SALCARE® SC 92" by the company ALLIED COLLOIDS. It is also possible to employ a crosslinked methacryloyloxyethyltrimethylammonium chloride homopolymer containing approximately 50% by weight of the

homopolymer in mineral oil or in a liquid ester. These dispersions are marketed under the names of "SALCARE® SC 95" and "SALCARE® SC 96" by the company ALLIED COLLOIDS.

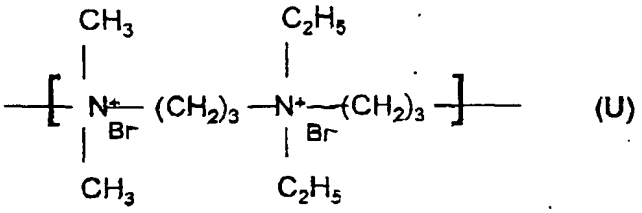
Other cationic polymers that may be employed within the scope of the invention are polyalkyleneimines, in particular polyethyleneimines, polymers containing vinylpyridine or vinylpyridinium units, condensates of polyamines and of epichlorohydrin, quaternary polyureylenes and chitin derivatives.

Among all the cationic polymers which may be used in the context of the present invention, it is preferable to use the polymers of the families (1), (9), (10), (11) and (14) and more preferably still the polymers with the repeat units of the following formulae (W) and (U):



(W)

and in particular those whose molecular weight, determined by gel permeation chromatography, is between 9 500 and 9 900;



(U)

and in particular those whose molecular weight, determined by gel permeation chromatography, is about 1 200.

The additional cationic polymer concentration in the composition according to the present invention may vary from 0.01 to 10% by weight relative to the total weight of the composition, preferably from 0.05 to 5% and more preferably still from 0.1 to 3%.

According to a second preferred embodiment, the composition according to the present invention additionally contains at least one thickening polymer also called "rheology-adjusting agents".

The additional rheology-adjusting agents may be chosen from fatty acid amides (diethanol- or monoethanolamide of copra,

monoethanolamide of oxyethylenated alkyl ether carboxylic acid), cellulosic thickeners (hydroxyethycellulose, hydroxypropylcellulose, carboxymethylcellulose), guar gum and its derivatives (hydroxypropylguar), gums of microbial origin (xanthan gum, scleroglucan gum), crosslinked homopolymers of acrylic acid or of acrylamidopropanesulphonic acid and the additional associative polymers as described below.

The associative polymers which can be used according to the invention are water-soluble polymers which are capable, in an aqueous medium, of reversibly combining with each other or with other molecules. These polymers are different from the polymers containing a fatty chain which are useful in the compositions according to the present application.

Their chemical structure comprises hydrophilic regions, and hydrophobic regions which are characterized by at least one fatty chain.

The additional associative polymers which can be used according to the invention may be of the anionic, cationic, amphoteric and preferably nonionic type.

Their concentration by weight in the dyeing composition may vary from about 0.01 to 10% of the total weight of the composition and in the ready-to-use composition (comprising the oxidizing agent) from about 0.0025 to 10% of the total weight of the composition. More preferably, this quantity varies from about 0.1 to 5% by weight in the dyeing composition and from about 0.025 to 10% in the ready-to-use composition.

Among the associative polymers of the anionic type, there may be mentioned:

-(I) the terpolymers of maleic anhydride/C_{30}-C_{38} α-olefin/alkyl maleate such as the product (maleic anhydride/C_{30}-C_{38} α-olefin/isopropyl maleate copolymer) sold under the name PERFORMA V 1608® by the company NEWPHASE TECHNOLOGIES.

-(II) the acrylic terpolymers comprising:

(a) about 20% to 70% by weight of a carboxylic acid with α,β-monoethylenic unsaturation,

(b) about 20 to 80% by weight of a nonsurfactant monomer with α,β-monoethylenic unsaturation different from (a),

(c) about 0.5 to 60% by weight of a nonionic monourethane which is the product of the reaction of a monohydric surfactant with a monoisocyanate with monoethylenic unsaturation,

such as those described in patent application EP-A-0 173 109 and more particularly that described in Example 3, namely a methacrylic acid/methyl acrylate/dimethyl metaisopropenyl benzyl isocyanate of ethoxylated (40 EO) behenyl alcohol terpolymer in 25% aqueous dispersion.

-(III) the copolymers comprising among their monomers a carboxylic acid with α,β-monoethylenic unsaturation and an ester of a carboxylic acid with α,β-monoethylenic unsaturation and an oxyalkylenated fatty alcohol.

Preferably, these compounds also comprise, as monomer, an ester of a carboxylic acid with α,β-monoethylenic unsaturation and a C_1-C_4 alcohol.

By way of example of this type of compound, there may be mentioned ACULYN 22® sold by the company ROHM and HAAS, which is an oxyalkylenated stearyl methacrylate/ethyl acrylate/methacrylic acid terpolymer.

Among the additional associative polymers of the cationic type, there may be mentioned polyacrylates containing non-cyclic amino side groups.

The additional associative polymers of the known ionic type which can be used according to the invention are preferably chosen from:

-(1) celluloses modified by groups comprising at least one fatty chain;

there may be mentioned by way of example:

- the hydroxyethylcelluloses modified by groups comprising at least one fatty chain such as alkyl, arylalkyl or alkylaryl groups, or mixtures thereof, and in which the alkyl groups are preferably C_8-C_{22}, such as the product NATROSOL PLUS GRADE 330 CS® (C_{16} alkyls) sold by the company AQUALON, or the product BERMOCOLL EHM 100® sold by the company BEROL NOBEL,

- those modified by polyalkylene glycol ether of alkylphenol groups, such as the product AMERCELL POLYMER HM-1500® (polyethylene glycol (15) ether of nonylphenol) sold by the company AMERCHOL.

-(2) hydroxypropylguars modified by groups comprising at least one fatty chain such as the product ESAFLOR HM 22® (C_{22} alkyl chain) sold by the company LAMBERTI, the products RE210-18® (C_{14} alkyl chain) and RE205-1® (C_{20} alkyl chain) sold by the company RHONE POULENC.

-(3) copolymers of vinylpyrrolidone and of hydrophobic monomers having a fatty chain, of which there may be mentioned by way of example:

- the products ANTARON V216® or GANEX V216® (vinylpyrrolidone/hexadecene copolymer) sold by the company I.S.P.

- the products ANTARON V220® or GANEX V220® (vinylpyrrolidone/eicosene copolymer) sold by the company I.S.P.

-(4) copolymers of C_1-C_6 alkyl methacrylates or acrylates and of amphiphilic monomers comprising at least one fatty chain such as for example the oxyethylenated stearyl acrylate/methyl acrylate copolymer sold by the company GOLDSCHMIDT under the name ANTIL 208®.

-(5) copolymers of hydrophilic methacrylates or acrylates and of hydrophobic monomers comprising at least one fatty chain such as for example the polyethylene glycol methacrylate/lauryl methacrylate copolymer.

-(6) polyether-polyurethanes comprising in their chain both hydrophilic sequences which are most often of a polyoxyethylenated nature and hydrophobic sequences which may be aliphatic chains alone and/or cycloaliphatic and/or aromatic chains.

-(7) polymers containing an aminoplast ether backbone possessing at least one fatty chain, such as the compounds PURE THIX® provided by the company SUD-CHEMIE.

Preferably, the polyether-polyurethanes comprise at least two lipophilic hydrocarbon chains, having from 6 to 30 carbon atoms, separated by a hydrophilic sequence, it being possible for the hydrocarbon chains to be pendent chains or chains at the end of a hydrophilic sequence. In particular, it is possible for one or more pendent chains to be envisaged. In addition, the polymer may comprise a hydrocarbon chain at one end or at both ends of a hydrophilic sequence.

The polyether-polyurethanes may be polyblocks, in particular in triblock form. The hydrophobic sequences may be at each end of the

chain (for example: triblock copolymer with hydrophilic central sequence) or distributed both at the ends and in the chain (polyblock copolymer for example). These same polymers may also be in the form of graft units or may be star-shaped.

The nonionic polyether-polyurethanes containing a fatty chain may be triblock copolymers whose hydrophilic sequence is a polyoxyethylenated chain comprising from 50 to 1 000 oxyethylenated groups. Nonionic polyether-polyurethanes comprise a urethane bond between the hydrophilic sequences, hence the origin of the name.

By extension, those whose hydrophilic sequences are linked by other chemical bonds to the lipophilic sequences are also included among the nonionic polyether-polyurethanes containing a fatty chain.

By way of examples of nonionic polyether-polyurethanes containing a fatty chain which can be used in the invention, it is also possible to use Rhéolate 205® containing a urea functional group sold by the company RHEOX or the Rhéolates® 208, 204 or 212, as well as Acrysol RM 184®.

There may also be mentioned the product ELFACOS T210® containing a C_{12-14} alkyl chain and the product ELFACOS T212® containing a C_{18} alkyl chain from AKZO.

The product DW 1206B® from RHOM & HAAS containing a C_{20} alkyl chain and with a urethane bond, sold at 20% dry matter content in water, may also be used.

It is also possible to use solutions or dispersions of these polymers in particular in water or in an aqueous alcoholic medium. By way of example of such polymers, there may be mentioned Rhéolate® 255, Rhéolate® 278 and Rhéolate® 244 sold by the company RHEOX. It is also possible to use the product DW 1206F and DW 1206J provided by the company ROHM & HAAS.

The polyether-polyurethanes which can be used according to the invention are in particular those described in the article by G. Fonnum, J. Bakke and Fk. Hansen - Colloid Polym. Sci 271, 380-389 (1993).

Still more particularly it is preferable to use a polyether-polyurethane which can be obtained by polycondensation of at least three compounds comprising (i) at least one polyethylene glycol comprising from 150 to 180 mol of ethylene oxide, (ii) stearyl alcohol or decyl alcohol and (iii) at least one diisocyanate.

Such polyether-polyurethanes are sold in particular by the company ROHM & HAAS under the names Aculyn 46® and Aculyn 44® [ACULYN 46® is a polycondensate of polyethylene glycol containing 150 or 180 mol of ethylene oxide, stearyl alcohol and methylenebis(4-cyclohexyl isocyanate) (SMDI), at 15% by weight in a matrix of maltodextrin (4%) and water (81%); ACULYN 44® is a polycondensate of polyethylene glycol containing 150 or 180 mol of ethylene oxide, decyl alcohol and methylenebis(4-cyclohexyl isocyanate) (SMDI), at 35% by weight in a mixture of propylene glycol (39%) and water (26%)].

According to a third preferred embodiment, the composition according to the present invention additionally contains at least one surfactant.

The surfactants which are suitable for carrying out the present invention are in particular the following:

(i) Anionic surfactant(s):

By way of example of anionic surfactants which can be used, alone or as mixtures, in the context of the present invention there may be mentioned in particular (nonlimiting list) the salts (in particular alkali metal, especially sodium, salts, ammonium salts, amine salts, amino alcohol salts or magnesium salts) of the following compounds: alkyl sulphates, alkyl ether sulphates, alkylamido ether sulphates, alkylarylpolyether sulphates, monoglyceride sulphates; alkyl sulphonates, alkyl phosphates, alkylamidesulphonates, alkyl aryl sulphonates, α-olefinsulphonates, paraffinsulphonates; (C_6-C_{24})alkyl sulphosuccinates, (C_6-C_{24})alkyl ether sulphosuccinates, (C_6-C_{24})alkylamide sulphosuccinates; (C_6-C_{24})alkyl sulphoacetates; (C_6-C_{24})acyl sarcosinates and (C_6-C_{24})acyl glutamates. It is also possible to use (C_6-C_{24})alkyl polyglycoside carboxylic esters such as alkyl glucoside citrates, alkyl polyglycoside tartrate and alkyl polyglycoside sulphosuccinates, alkyl sulphosuccinamates; acyl isethionates and N-acyltaurates, the alkyl or acyl radical of all these various compounds preferably comprising from 12 to 20 carbon atoms, and the aryl radical preferably denoting a phenyl or benzyl group. Among the anionic surfactants which can still be used, there may also be mentioned the salts of fatty acids such as the salts of oleic, ricinoleic, palmitic and stearic acids, the acids of copra oil or of hydrogenated copra oil; the acyllactylates whose acyl radical comprises 8 to 20 carbon atoms. It is

also possible to use the alkyl D-galactoside uronic acids and their salts, the polyoxyalkylenated (C_6-C_{24})alkyl ether carboxylic acids, the polyoxyalkylenated (C_6-C_{24})alkylaryl ether carboxylic acids, the polyoxyalkylenated (C_6-C_{24})alkyl amido ether carboxylic acids and their salts, in particular those comprising from 2 to 50 alkylene, in particular ethylene, oxide groups, and mixtures thereof.

(ii) Nonionic surfactant(s):

The nonionic surfactants themselves are also compounds which are well known per se (in this respect see especially the "Handbook of Surfactants" by M.R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178) and, in the context of the present invention, their nature does not assume any critical character. They can thus be chosen especially from (nonlimiting list) alcohols, alpha-diols or polyethoxylated or polypropoxylated alkylphenols which have a fatty chain containing, for example, 8 to 18 carbon atoms, it being possible for the number of ethylene oxide or propylene oxide groups to range especially from 2 to 50. The copolymers of ethylene oxide and propylene oxide and the condensates of ethylene oxide and propylene oxide with fatty alcohols may also be mentioned; the polyethoxylated fatty amides preferably containing from 2 to 30 mol of ethylene oxide, the polyglycerolated fatty amides containing on average 1 to 5 glycerol groups and in particular 1.5 to 4; the oxyethylenated fatty acid esters of sorbitan containing from 2 to 30 mol of ethylene oxide; the fatty acid esters of sucrose, the fatty acid esters of polyethylene glycol, alkylpolyglycosides, the N-alkylglucamine derivatives, amine oxides such as the oxides of (C10-C14)alkylamines or the N-acylaminopropylmorpholine oxides.

(iii) Amphoteric or zwitterionic surfactant(s):

The amphoteric or zwitterionic surfactants, the nature of which is not of critical importance in the context of the present invention, may be especially (nonlimiting list) derivatives of aliphatic secondary or tertiary amines in which the aliphatic radical is a linear or branched chain containing 8 to 18 carbon atoms and containing at least one water-solubilizing anionic group (for example carboxylate, sulphonate, sulphate, phosphate or phosphonate); (C_8-C_{20})alkylbetaines, sulphobetaines, (C_8-C_{20})alkylamido(C_1-C_6)alkylbetaines or (C_8-C_{20})alkylamido(C_1-C_6)alkylsulphobetaines may further be mentioned.

Among the amine derivatives, there may be mentioned the products sold under the name MIRANOL, as described in patents US-2 528 378 and US-2 781 354 and classified in the CTFA dictionary, 3rd edition, 1982, under the names Amphocarboxyglycinates and Amphocarboxypropionates having the respective structures:

R_2-$CONHCH_2CH_2$-$N(R_3)(R_4)(CH_2COO^-)$

in which: R2 denotes an alkyl radical of an acid R_2-COOH present in hydrolysed copra oil, a heptyl, nonyl or undecyl radical, R3 denotes a beta-hydroxyethyl group and R_4 a carboxymethyl group;

and

R_2'-$CONHCH_2CH_2$-N(B)(C)

in which:

B represents $-CH_2CH_2OX'$, C represents $-(CH_2)_z-Y'$, with z = 1 or 2,

X' denotes the $-CH_2CH_2-COOH$ group or a hydrogen atom

Y' denotes -COOH or the radical $-CH_2-CHOH-SO_3H$

R_2' denotes an alkyl radical of an acid R_9 -COOH present in copra oil or in hydrolysed linseed oil, an alkyl radical, especially C_7, C_9, C_{11} or C_{13}, a C_{17} alkyl radical and its iso form or an unsaturated C_{17} radical.

These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names Disodium Cocoamphodiacetate, Disodium Lauroamphodiacetate, Disodium Caprylamphodiacetate, Disodium Capryloamphodiacetate, Disodium Cocoamphodipropionate, Disodium Lauroamphodipropionate, Disodium Caprylamphodipropionate, Disodium Capryloamphodipropionate, Lauro amphodipropionic acid, Cocoamphodipropionic acid.

By way of example, there may be mentioned the cocoamphodiacetate marketed under the trade name MIRANOL® C2M concentrated by the company RHODIA CHIMIE.

(iv) Cationic surfactants:

Among the cationic surfactants, there may be mentioned in particular (nonlimiting list): the salts of optionally polyoxyalkylenated primary, secondary or tertiary amines; quaternary ammonium salts such as tetraalkylammonium, alkylamidoalkyltrialkylammonium, trialkylbenzylammonium, trialkylhydroxyalkylammonium or alkylpyridinium chlorides or bromides; imidazoline derivatives or amine oxides of a cationic nature.

The quantities of surfactants present in the composition according to the invention may vary from 0.01 to 40% and preferably from 0.5 to 30% of the total weight of the composition.

The composition of the present invention may additionally comprise one or more additional oxidation bases which are conventionally used in oxidation dyeing other than the para-phenylenediamines of formula I. By way of example, these additional oxidation bases are chosen from phenylenediamines, bisphenylalkylenediamines, para-aminophenols, ortho-aminophenols, heterocyclic bases other than the heterocyclic para-phenylenediamines and their addition salts.

Among the para-phenylenediamines, there may be mentioned, by way of example, para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-2-chloroaniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl-β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2-β-acetylaminoethyloxy-para-phenylenediamine, N-(β-methoxyethyl)-para-phenylenediamine, 4-aminophenylpyrrolidine, 2-thienyl-para-phenylenediamine, 2-β-hydroxyethylamino-5-aminotoluene, 3-hydroxy-1-(4'-aminophenyl)pyrrolidine and their addition salts with an acid.

Among the para-phenylenediamines mentioned above, there are particularly preferred para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2-β-hydroxyethyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-

phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine, 2-β-acetylaminoethyloxy-para-phenylenediamine, and their addition salts with an acid.

Among the bisphenylalkylenediamines, there may be mentioned, by way of example, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)-tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine, 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane, and their addition salts.

Among the para-aminophenols, there may be mentioned, by way of example, para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-chlorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β-hydroxyethylaminomethyl)phenol, 4-amino-2-fluorophenol, and their addition salts with an acid.

Among the ortho-aminophenols, there may be mentioned, by way of example, 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 5-acetamido-2-aminophenol, and their addition salts.

Among the heterocyclic bases, there may be mentioned, by way of example, pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

Among the pyridine derivatives, there may be mentioned the compounds described for example in patents GB 1 026 978 and GB 1 153 196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 3,4-diaminopyridine, and their addition salts.

Other pyridine oxidation bases useful in the present invention are the oxidation bases 3-aminopyrazolo[1,5-a]pyridines or their addition salts which are described, for example, in patent application FR 2801308. By way of example, there may be mentioned pyrazolo[1,5-a]pyridin-3-ylamine; 2-acetylaminopyrazolo[1,5-a]pyridin-3-ylamine; 2-morpholin-4-ylpyrazolo[1,5-a]pyridin-3-ylamine; 3-aminopyrazolo[1,5-a]pyridine-2-carboxylic acid;

2-methoxypyrazolo[1,5-a]pyridin-3-ylamino; (3-aminopyrazolo[1,5-a]pyridin-7-yl)methanol; 2-(3-aminopyrazolo[1,5-a]pyridin-5-yl)ethanol; 2-(3-aminopyrazolo[1,5-a]pyridin-7-yl)ethanol; (3-aminopyrazolo[1,5-a]pyridin-2-yl)methanol; 3,6-diaminopyrazolo[1,5-a]pyridine; 3,4-diaminopyrazolo[1,5-a]pyridine; pyrazolo[1,5-a]pyridine-3,7-diamine; 7-morpholin-4-ylpyrazolo[1,5-a]pyridin-3-ylamine; pyrazolo[1,5-a]pyridine-3,5-diamine; 5-morpholin-4-ylpyrazolo[1,5-a]pyridin-3-ylamine; 2-[(3-aminopyrazolo[1,5-a]pyridin-5-yl)(2-hydroxyethyl)amino]ethanol; 2-[(3-aminopyrazolo[1,5-a]pyridin-7-yl)(2-hydroxyethyl)amino]ethanol, 3-aminopyrazolo[1,5-a]pyridin-5-ol; 3-aminopyrazolo[1,5-a]pyridin-4-ol, 3-aminopyrazolo[1,5-a]pyridin-6-ol; 3-aminopyrazolo[1,5-a]pyridin-7-ol; and their addition salts.

Among the pyrimidine derivatives, there may be mentioned the compounds described for example in patents DE 2 359 399; JP 88-169 571; JP 05-63124; EP 0 770 375 or patent application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2,5,6-triaminopyrimidine, and their addition salts and their tautomeric forms, when a tautomeric equilibrium exists.

Among the pyrazole derivatives, there may be mentioned the compounds described in patents DE 3 843 892, DE 4 133 957 and patent applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988 such as 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole,

1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole, 3,5-diamino-4-(β-hydroxyethyl)amino-1-methylpyrazole, and their addition salts.

The additional oxidation base(s) present in the composition of the invention are generally present in a quantity of between 0.001 to 20% by weight approximately of the total weight of the dyeing composition, preferably between 0.005 and 6%.

The composition according to the invention preferably contains, one or more additional couplers conventionally used for dyeing keratinous fibres. Among these couplers, there may be mentioned in particular meta-phenylenediamines, meta-diphenols, naphthalene couplers, heterocyclic couplers and their addition salts.

By way of example, there may be mentioned 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β-hydroxyethyloxy)benzene, 2-amino-4-(β-hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-dimethylaminobenzene, sesamol, 1-β-hydroxyethylamino-3,4-methylenedioxybenzene, α-naphthol, 2-methyl-1-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 1-N-(β-hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-bis(β-hydroxyethylamino)toluene and their addition salts.

In the composition of the present invention, the coupler(s) are generally present in a quantity of between 0.001 and 20% by weight approximately of the total weight of the dyeing composition, preferably ranging from 0.005 to 6%.

In general, the addition salts of the oxidation bases and couplers which can be used in the context of the invention are in particular chosen from the addition salts with an acid such as the hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates, tosylates, benzenesulphonates, phosphates and acetates and the addition salts with a base such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, amines or alkanolamines.

The dyeing composition in accordance with the invention may additionally contain one or more direct dyes which may be chosen in particular from neutral, acidic or cationic nitro dyes of the benzene

series, neutral, acidic or cation azo direct dyes, neutral, acidic or cationic quinone and in particular antraquinone direct dyes, azine direct dyes, triarylmethane direct dyes, indoamine direct dyes and natural direct dyes.

Among the benzene direct dyes which can be used according to the invention, the following compounds may be mentioned without limitation:

- 1,4-diamino-2-nitrobenzene,
- 1-amino-2 nitro-4-ß- hydroxyethylaminobenzene
- 1-amino-2 nitro-4-bis(β-hydroxyethyl)aminobenzene
- 1,4-bis(ß-hydroxyethylamino)-2-nitrobenzene
- 1-ß-hydroxyethylamino-2-nitro-4-bis-(β-hydroxyethylamino)benzene
- 1-ß-hydroxyethylamino-2-nitro-4-aminobenzene
- 1-β-hydroxyethylamino-2-nitro-4-(ethyl)(ß-hydroxyethyl)aminobenzene
- 1-amino-3-methyl-4-β-hydroxyethylamino-6-nitrobenzene
- 1-amino-2-nitro-4-β-hydroxyethylamino-5-chlorobenzene
- 1,2-diamino-4-nitrobenzene
- 1-amino-2-β-hydroxyethylamino-5-nitrobenzene
- 1,2-bis(β-hydroxyethylamino)-4-nitrobenzene
- 1-amino-2-tris-(hydroxymethyl)methylamino-5-nitrobenzene
- 1-hydroxy-2-amino-5-nitrobenzene
- 1-hydroxy-2-amino-4-nitrobenzene
- 1-hydroxy-3-nitro-4-aminobenzene
- 1-hydroxy-2-amino-4,6-dinitrobenzene
- 1-β-hydroxyethyloxy-2-β-hydroxyethylamino-5-nitrobenzene
- 1-methoxy-2-β-hydroxyethylamino-5-nitrobenzene
- 1-β-hydroxyethyloxy-3-methylamino-4-nitrobenzene
- 1- β,γ-dihydroxypropyloxy-3-methylamino-4-nitrobenzene
- 1-β-hydroxyethylamino-4-β,γ-dihydroxypropyloxy-2-nitrobenzene
- 1-β,γ-dihydroxypropylamino-4-trifluoromethyl-2-nitrobenzene
- 1-β-hydroxyethylamino-4-trifluoromethyl-2-nitrobenzene
- 1-β-hydroxyethylamino-3-methyl-2-nitrobenzene
- 1-β-aminoethylamino-5-methoxy-2-nitrobenzene
- 1-hydroxy-2-chloro-6-ethylamino-4-nitrobenzene

- 1-hydroxy-2-chloro-6-amino-4-nitrobenzene
- 1-hydroxy-6-bis-(β-hydroxyethyl)amino-3-nitrobenzene
- 1-β-hydroxyethylamino-2-nitrobenzene
- 1-hydroxy-4-β-hydroxyethylamino-3-nitrobenzene.

Among the azo direct dyes which can be used according to the invention, there may be mentioned the cationic azo dyes described in patent applications WO 95/15144, WO 95/01772 and EP-714954 whose content forms an integral part of the invention.

Among these compounds the following dyes may be most particularly mentioned:

- 1,3-dimethyl-2-[[4-(dimethylamino)phenyl]azo]-1H-imidazolium chloride,
- 1,3-dimethyl-2-[(4-aminophenyl)azo]-1H-imidazolium chloride,
- 1-methyl-4-[(methylphenylhydrazono)methyl]pyridinium methyl sulphate.

There may also be mentioned, among the azo direct dyes, the following dyes, which are described in COLOUR INDEX INTERNATIONAL 3rd edition:

-Disperse Red 17
-Acid Yellow 9
-Acid Black 1
-Basic Red 22
-Basic Red 76
-Basic Yellow 57
-Basic Brown 16
-Acid Yellow 36
-Acid Orange 7
-Acid Red 33
-Acid Red 35
-Basic Brown 17
-Acid Yellow 23
-Acid Orange 24
-Disperse Black 9.

There may also be mentioned 1-(4'-aminodiphenylazo)-2-methyl-4bis(β-hydroxyethyl) aminobenzene and 4-hydroxy-3-(2-methoxyphenylazo)-1-naphtalenesulphonic acid.

Among the quinone direct dyes, the following dyes may be mentioned:

-Disperse Red 15

-Solvent Violet 13

-Acid Violet 43

-Disperse Violet 1

-Disperse Violet 4

-Disperse Blue 1

-Disperse Violet 8

-Disperse Blue 3

-Disperse Red 11

-Acid Blue 62

-Disperse Blue 7

-Basic Blue 22

-Disperse Violet 15

-Basic Blue 99

and the following compounds:

-1-N-methylmorpholiniumpropylamino-4-hydroxyanthraquinone

-1-aminopropylamino-4-methylaminoanthraquinone

-1-aminopropylaminoanthraquinone

-5-β-hydroxyethyl-1,4-diaminoanthraquinone

-2-aminoethylaminoanthraquinone

-1,4-bis(β,γ-dihydroxypropylamino)anthraquinone.

Among the azine dyes, the following compounds may be mentioned:

-Basic Blue 17

-Basic Red 2.

Among the triarylmethane dyes which can be used according to the invention, the following compounds may be mentioned:

-Basic Green 1

-Acid blue 9

-Basic Violet 3

-Basic Violet 14

-Basic Blue 7

-Acid Violet 49

-Basic Blue 26

-Acid Blue 7

Among the indoamine dyes which can be used according to the invention, the following compounds may be mentioned:

- 2-β-hydroxyethylamino-5-[bis(β-4'-hydroxyethyl)amino]anilino-1,4-benzoquinone
- 2-β-hydroxyethylamino-5-(2'-methoxy-4'-amino)anilino-1,4-benzoquinone
- 3-N(2'-chloro-4'-hydroxy)phenylacetylamino-6-methoxy-1,4-benzoquinoneimine
- 3-N(3'-chloro-4'-methylamino)phenylureido-6-methyl-1,4-benzoquinoneimine
- 3-[4'-N-(ethylcarbamylmethyl)amino]phenylureido-6-methyl-1,4-benzoquinoneimine

Among the natural direct dyes which can be used according to the invention, there may be mentioned lawsone, juglone, alizarin, purpurin, carminic acid, kermesic acid, purpurogallin, protocatechaldehyde, indigo, isatin, curcumin, spinulosin and apigenidin. It is also possible to use extracts or decoctions containing these natural dyes and in particular henna-based poultices or extracts.

The direct dye(s) preferably represent from 0.001 to 20% by weight approximately of the total weight of the ready-to-use composition and still more preferably from 0.005 to 10% by weight approximately.

The composition according to the invention may also contain at least one hydroxylated solvent, such as in particular ethanol, propylene glycol, glycerol, polyol monoethers, benzyl alcohol.

It may also contain a nonhydroxylated solvent.

The hydroxylated solvents and the nonhydroxylated solvents are preferably present in proportions preferably between 1 and 40% by weight approximately relative to the total weight of the dyeing composition, and still more preferably between 5 and 30% by weight approximately.

The dyeing composition in accordance with the invention may also contain various adjuvants conventionally used in hair dyeing compositions, such as antioxidants, penetrating agents, sequestering agents, perfumes, buffers, dispersing agents, conditioning agents such as for example modified or unmodified, volatile or nonvolatile silicones, film-forming agents, ceramides, preservatives and opacifying agents.

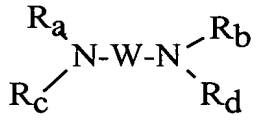
The above adjuvants are generally present in a quantity, for each of them, of between 0.01 and 20% by weight relative to the weight of the composition.

Of course, persons skilled in the art will be careful to choose this or these optional additional compounds such that the advantageous properties intrinsically attached to the oxidation dyeing composition in accordance with the invention are not, or not substantially, impaired by the addition(s) envisaged.

The pH of the dyeing composition in accordance with the invention is generally between 3 and 12 approximately, and preferably between 5 and 11 approximately. It may be adjusted to the desired value by means of acidifying or alkalinizing agents customarily used in dyeing keratinous fibres or with the aid of conventional buffering systems.

Among the acidifying agents, there may be mentioned, by way of example, inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid, lactic acid and sulphonic acids.

Among the alkalinizing agents, there may be mentioned, by way of example, ammonium hydroxide, alkali metal carbonates, alkanolamines such as mono-, di- and triethanolamines and the derivatives thereof, sodium or potassium hydroxides and the compounds of the following formula (XXIII):



(XXIII)

in which W is a propylene residue optionally substituted with a hydroxyl group or a C_1-C_4 alkyl radical; R_a, R_b, R_c and R_d, which may be identical or different, represent a hydrogen atom, a C_1-C_4 alkyl radical or a C_1-C_4 hydroxyalkyl radical.

The dyeing composition according to the invention may be provided in various forms, such as in the form of liquids, creams or gels, or in any other appropriate form for dyeing keratinous fibres, and in particular human hair.

The method of the present invention is a method in which the composition according to the present invention, as defined above, is

applied to the fibres, and the colour is developed using an oxidizing agent. The colour may be developed at acidic, neutral or alkaline pH and the oxidizing agent may be added to the composition of the invention just at the time of use or it can be used from an oxidizing composition containing it, applied simultaneously or sequentially with the composition of the invention.

According to a particular embodiment, the composition according to the present invention is mixed, preferably at the time of use, with a composition containing, in a medium appropriate for dyeing, at least one oxidizing agent, this oxidizing agent being present in a sufficient quantity to develop a colour. The mixture obtained is then applied to the keratinous fibres. After an exposure time of 3 to 50 minutes approximately, preferably 5 to 30 minutes approximately, the keratinous fibres are rinsed, washed with shampoo, rinsed again and then dried.

The oxidizing agents conventionally used for the oxidation dyeing of keratinous fibres are, for example, hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulphates, peracids and the oxidase enzymes, among which there may be mentioned peroxidases, oxidoreductases with 2 electrons such as uricases and oxygenases with 4 electrons such as laccases. Hydrogen peroxide is particularly preferred.

The oxidizing composition may also contain various adjuvants conventionally used in hair dyeing compositions and as defined above.

The pH of the oxidizing composition containing the oxidizing agent is such that, after mixing with the dyeing composition, the pH of the resulting composition applied to keratinous fibres preferably varies between 3 and 12 approximately, and still more preferably between 5 and 11. It may be adjusted to the desired value by means of acidifying or alkalinizing agents customarily used for dyeing keratinous fibres and as defined above.

The ready-to-use composition which is finally applied to the keratinous fibres may be provided in various forms, such as in the form of liquids, creams or gels, or in any other form appropriate for dyeing keratinous fibres, and in particular human hair.

The subject of the invention is finally a multicompartment device or dyeing "kit" in which a first compartment contains the dyeing composition defined above and a second compartment contains

an oxidizing composition. This device may equipped with means which make it possible to deliver the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the applicant.

Using this device, it is possible to dye keratinous fibres using a method which comprises mixing a dyeing composition in accordance with the invention with an oxidizing agent as defined above, and applying the mixture obtained to the keratinous fibres for a time sufficient to develop the desired colour.

DETAILED DESCRIPTION

The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

Example 1 :

Dyeing composition: (expressed in grams)

Oleyl alcohol	6
Oleic acid	3
Polyglycerolenated oleyl alcohol containing 2 moles of glycerol	6
Polyglycerolenated oleyl alcohol containing 6 moles of glycerol	6
Diethylaminopropyl laurylaminosuccinamate, sodium salt	3
Oxyethylenated oleyl amine containing 2 moles of ethylene oxide	7
Monoethanolamide of alkyl ether carboxylic acid containing 2 moles of ethylene oxide	10
Ammonium acetate	20
Hexylene glycol	20
Reducing agents, antioxidants	0.915
Sequestrants	1
[1-(4-aminophenyl)pyrrolidin-3-yl]trimethylammonium chloride	0.8
ACP 1234 (ISP)	0.2 A.M.
2-methyl-5-aminophenol	0.5

Perfume	qs
Ammonium hydroxide (containing 20.5% ammonia)	10.2
Demineralized water qs	100

At the time of use, this composition is mixed weight for weight with an oxidizing milk containing 6% hydrogen peroxide. The mixture obtained is applied for 30 minutes to grey hair which is 90% white. A purple brown coloration is obtained on this hair after rinsing, shampooing and drying.

Example 2 :

Dyeing composition: (expressed in grams)

Oleyl alcohol	4
Oleic acid	5
Polyglycerolenated oleyl alcohol containing 2 moles of glycerol	4
Polyglycerolenated lauryl alcohol containing 4 moles of glycerol	3.6
Oxyethylenated rape acid amide containing 4 moles of ethylene oxide	8
Oxyethylenated oleyl amine containing 2 moles of ethylene oxide	4
Oxyethylenated decyl alcohol containing 3 moles of ethylene oxide	2.7
Ethyl alcohol	7.45
Propylene glycol	15
Reducing agents, antioxidants	0.63
Sequestrant	1
3-[1-(4-aminophenyl)pyrrolidin-3-yl]-1-methyl-3H-imidazol-1-ium chloride	0.85
5N(β-hydroxyethyl)amino-2-methylphenol)	0.5
Cationic polyurethane obtained from the polycondensation of 1,3-bis(methylcyclohexane isocyanate), of N,N-dimethylethanolamine	0.25

quaternized with bromododecane, of N,N-dimethylethanolamine and of POE 10 000	
Pure monoethanolamine	2
Perfume	Qs
Ammonium hydroxide (containing 20.5% ammonia)	10
Demineralized water qs	100

At the time of use, this composition is mixed weight for weight with an oxidizing milk containing 6% hydrogen peroxide. The mixture obtained is applied for 30 minutes to grey hair which is 90% white. A deep purple coloration is obtained on this hair after rinsing, shampooing and drying.